TECHNOLOGY OF
CELLULOSE ESTERS

A THEORETICAL AND PRACTICAL TREATISE ON THE ORIGIN,
HISTORY, CHEMISTRY, MANUFACTURE, TECHNICAL APPLICATION AND ANALYSIS OF THE PRODUCTS OF ACYLATION AND
ALKYLATION OF NORMAL AND MODIFIED CELLULOSE, INCLUDING NITROCELLULOSE, CELLULOID, PYROXYLIN, COLLODION,
CELLOIDIN, GUNCOTTON, ACETYLCELLULOSE AND VISCOSE,
AS APPLIED TO TECHNOLOGY, PHARMACY, MICROSCOPY,
MEDICINE, PHOTOGRAPHY, AND THE WARLIKE
AND PEACEFUL ARTS

IN TEN VOLUMES

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This Table of Contents contains an enumeration of the 637 main topics only, the five hundred forty sub-topics not being indicated herein.

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ABBREVIATIONS.

A. A. A. S.	American Association for the Advancement of Science
Anon	Anonyme (Anonymous)
A. O. A. C.	Association of Official Agricultural Chemists
abs.	absolute
A. C.	Alternating current
Act.	Actien
Add.	Addition Patent
alc.	alcohol ethyl
alk.	alkaline
amp.	ampere
amt.	amount
approx.	approximate
at.	atom, atomic
atm.	atmosphere(s)
atm. pr.	atmospheric pressure
as-	assymmetric
av.	average
b.	boil(s), boiling
b. pt	boiling point
c.	asymmetric carbon atom
cal.	calorie
cc.	cubic centimeter(s)
chem.	chemical
C. I.	cast iron
com	commercial
comp.	composition
compd.	compound
conc.	concentrat-ed, ion
cor.	corrected
C. O. V.	Concentrated oil of vitriol
c. p.	candle power
crys.	crystals, crystallized
cu.	cubic
cu. ft.	cubic foot (feet)
cu. m.	cubic meter(s)
cwt.	hundredweight
D. C.	Direct current
d-	dextro
d.	density
diam.	diameter
dcm.	decimeter
dil.	dilute
dr.	dram
fl.	fluid
Farb.	Farbenfabriken
f. pt.	freezing point
gal.	U. S. gallon, 3785 cc.
Ges.	Gesellschaft
gm.	gram(s)
gr.	grain(s)
h. p.	horse power
hr.	hour(s)
insol.	insoluble
in.	inch
k.	kilogram
kw.	kilowatt
l.	liter(s)
l.	laevo
lab.	laboratory
lb.	Avoirdupois pound(s)
Ltd.	Limited
m.	meter
m.	meta
mfr.	manufacturer
mfg.	manufacturing
mgm.	milligram
min.	minute(s)
mm.	millimeter
mol.	molecule(s)
mol. wt.	molecular weight
m. pt.	melting point
M. S.	Mild steel
nor.	normal
n. t. p.	normal temperature and pressure (0° C, 760 mm.)
o-	ortho
ord.	ordinary
oz.	Avoirdupois ounce
p-	para
pp.	precipitate
p.	pint
qt.	quart
quant.	quantitative
recryst.	recrystallized
r. p. m.	revolution per minute
sat.	saturate(d)
sc.	scruple
sec.	second(s)
soln.	solution
Soc.	Societe
sp. gr.	specific gravity
sq.	square
S. T. P.	Standard temperature (15.56° C.) and pressure (760 mm.)
sym.	symmetrical
temp.	temperature(s)
v-	vicinal
vac.	vacuum
vol.	volume(s)
wt.	weight
°	degrees Centigrade (always)
%	per cent. by weight

TABLE OF SUMMARIES TO VOLUME ONE

Chapt	Pages	Topics	Tables	Cuts	Foot Notes	Patents	Literature References	Names
I	388	75	32	0	1124	3624	13665	5042
II	96	19	2	0	798	896	6583	1839
III	98	27	19	1	174	143	565	211
IV	82	11	0	40	111	238	508	466
V	344	71	1	41	1199	5116	10386	4994
VI	396	141	13	25	1676	4609	9376	5911
VII	116	21	2	30	100	111	509	155
VIII	48	0	34	0	12	—	7	20
IX	366	65	33	3	1420	1175	8359	1988
X	340	54	11	138	320	577	1014	351
XI	104	27	3	14	204	6	1216	302
XII	707	88	0	2	12473	22963	28316	12461
Total	3085	599	150	294	19611	39458	80504	33740

LIST OF ABBREVIATIONS TO LITERATURE

Prepared by Dr. Carl Marx

A. and N. J.	Army and Naval Journal
Aarau, Archiv der Med.	Archiv. der Medizin, Chirurgie, und Pharmazie
Aarau, Mitth.	Mittheilungen des Aargauischen Naturforschenden Gesellschaft
Abbeville, Bull. Soc. Linn.	Compte Rendu et Bulletin de la Société Linneenne du Nord de la France
Abbeville, Mem. Soc Emul.	Memoires de la Société d'Emulation d'Abbeville
Abeille, J.	L'Abeille, Journal d'Entomologie
Abeille mem.	L'Abeille: memoires d'Entomologie
Abeille Soc.	(Publications de la Soc. Entomologie de France.) LaAbeille. Journal de Entomologie
Acad.	Memoires de l'Academie des Sciences
Acad. Caes. Leop. Nova Acta	Nova Acta physico-medica Academiae Caes. Leopoldino-Carolinae Naturae Curiosorum
Acad. Natur. Curios. Nova Acta	Nova Acta Academiae Caesareae Leopoldino-Carolinae Germanicae Naturae Curiosorum
Acireale Accad. Atti	Atti e Rendiconti dell' Accademia di Scienze, Lettere e Arti dei Zelanti e PP. dello Studio di Acireale
Acireale, Soc. Ital. Micro. Boll.	Bollettino della Societa Italiana dei Microscopisti
Acquoy, Tijdschrift	Tijdschrift voor Wis-, Natuur-, en Wertuigkunde
Acta Math.	Acta Mathematica
Actes Soc. Helvetique	Actes de la Société Helvétique des Sciences Naturelles
Adansonia	Adansonis: Recueil d'observations botaniques
Adelaide Phil. Soc. Trans.	Transactions and Proceedings and Report of the Philosophical Society of Adeliade, South Australia
Aeronaut. J.	The Aeronautical Journal
Aeronaut. Soc. Reports	Annual Reports of the Aeronautical Society of Great Britain
Aeronaute	L'Aeronaute: bulletin mensuel international de la Navigation Aerienne
Afhandl. Fysik.	Afhandlingar i Fysik, Kemi, och Mineralogi
African Assoc. Proc.	Proceedings of the African Association for promoting the Discovery of the Interior Parts of Africa
Agen, Soc. Agric. Recueil.	Recueil des Travaux de la Société d'Agriculture, Sciences, et Arts d'Agen
Agram., Program Gymnas.	Program des k. k. Akademischen Gymnasiums zu Agram
Agric. Gaz.	The Agricultural Gazette
Agric. Gaz. N. S. Wales	Agricultural Gazette of New South Wales, The
Agric. J. India	Agricultural Journal of India
Agric. Ledg.	Agricultural Ledger
Agric. Soc. J.	The Journal of the Royal Agricultural Society of England
Agric. Stud. Gaz.	Agricultural Students' Gazette. A Quarterly Journal edited by Students at the College, Cirencester
Agron. Ztg.	Agronomische Zeitung
Aix. Acad. Mem.	Recueil de Memoires de la Société des Amis des Sciences, des Lettres, de l'Agricultur, et des Arts a Aix

Albany Inst. Proc.	Proceedings of the Albany Institute
Albany Inst. Trans.	Transactions of the Albany Institute
Alger. Bull. Soc. Climat.	Bulletin de la Societe de Climatologie Algerienne
Alk.	Alkohol
Allelod. Soc. Trans.	The transaction of the Allelodidactic Society
Allg. Berg. Ztg.	Allgemeine berg- und hüttenmännische Zeitung
Allg. Bot. Zts.	Allgemeine Botanische Zeitscrift fur Systematik, Floristik, Pflanzengeographie, etc.
Allg. Deut. Naturhist. Ztg.	Allgemeine Deutsche naturhistorische Zeitung
Allg. Deut. Ornith. Ges.	See J. Ornith
Allg. Fischerei Ztg.	Allgemeine Fischerei Zeitung
Allg. Forst-Jagd-Zts.	Allgemeine Forst- und Jagd-Zeitung
Allg. Gerber-Ztg.	Allgemeine Gerber-Zeitung
Allg. Schweiz. Ges. Gesam. Naturwiss.	See Zürich, Schweiz. Ges. N. Denkschr.
Allg. Syn. Suikerfab.	Algemeen Syndicat van Suikerfabrikanten in Nederl.-Indie. With Arch-Suikerind, etc.
Allg. Zts. Bierbr. Malzfabr.	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation
Allier, Bull. Soc. Emul.	Bulletin de las Société d'Émulation du département de l'Allier: Sciences, Arts, et Belles-Lettres
Alpina	Alpina, eine Schrift der genauen Kenntniss der Alpen gewidmet; von Carl Ulisses von Salis und J. R. Steinmueller
Altenburg Mitth.	Mittleilungen aus dem Osterlande; herausgegeben von der Naturforschenden Gesellschaft zu Altenburg
Amat. Mechan. Soc. J.	The (Quarterly) Journal of the Amateur Mechanical Society
Amer. Acad. Mem.	Memoirs of the American Academy of Arts and Sciences
Amer. Acad. Proc.	Proceedings of the American Academy of Arts and Sciencess
Amer. Agric.	American Agriculturist
Amer. Ann. Phot.	American Annual of Photography
Amer. Apoth. Ztg.	Deutsch-Amerikanische Apotheker Zeitung
Amer. Artisan	American Artisan
Amer. Assoc. Proc.	Proceedings of the American Association for the Advancement of Science
Amer. Brewers Rev.	American Brewers Review
Amer. Builder	The American Builder
Amer. Chem. J.	American Chemical Journal
Amer. Chemist	American Chemist
Amer. Drug.	American Druggist and Pharmaceutical Record
Amer. Electrochem. Soc	American Electrochemical Society
Amer. Engin. & Railroad J.	American Engineer (Car Builder), and Railroad Journal
Amer. Ethnol. Soc. Trans.	Transactions of the American Ethnological Society
Amer. Entom. Soc. Trans.	Transactions of the American Entomological Society and Proceedings of the Entomological Section of the Academy of Natural Sciences
Amer. Fertilizer	American Fertilizer, The
Amer. Food J.	American Food Journal
Amer. Gas Light J.	American Gas Light Journal, The
Amer. Geogr. Soc. Bull.	Bulletin of the American Geographical and Statistical Society
Amer. Geogr. Soc. J.	Journal American Geographical Society, New York
Amer. Geogr. Soc. Proc.	Proceedings of the American Geographical and Statistical Society of New York

Amer. Geol. and Nat. Assoc. Reports	Reports of the Meetings of the Association of American Geologists and Naturalists at Philadelphia
Amer. J. Conchol.	American Journal of Conchology
Amer. J. Dent. Sci.	American Journal of Dental Science
Am. J. Math.	American Journal of Mathematics
Amer. J. Med. Sci.	American Journal of the Medical Sciences
Amer. J. Otol.	The American Journal of Otology
Amer. J. Pharm.	American Journal of Pharmacy
Amer. J. Physiol.	The American Journal of Physiology
Amer. J. Physiol., Boston	American Journal of Physiology, Boston
Amer. J. Psychol.	The American Journal of Psychology
Amer. J. Pub. Health	American Journal of Public Health
Amer. J. Sci.	The American Journal of Science
Amer. Mach.	American Machinist
Amer. Math. Soc.	See N. Y. Amer. Math Soc.
Amer. Med.	American Medicine
Amer. Med. Assoc. Trans.	Transactions of the American Medical Association
Amer. Med. Phil. Reg.	The American Medical and Philosophical Register; or Annals of Medicine, Natural History, Agriculture, and the Arts
Amer. Med. Recorder	American Medical Recorder
Amer. Meteorol. J.	American Meteorological Journal
Amer. Micro J.	The American Quarterly Microscopical Journal. With which is also published the Transaction of the New York Microscopical Society
Amer. Micro Soc. Proc.	Proceedings of the American Microscopical Society
Amer. Micro. Soc. Trans.	Transactions of the American Microscopical Society
Amer. Mineral J.	The American Mineralogical Journal
Amer. Min Gaz.	The American Mining Gazette and Geological Magazine
Amer. Monthly Micro. J.	American Monthly Microscopical Journal
Amer. Mus. Bull.	Bulletin of the American Museum of Natural Histor
Amer. Mus. Mem.	Memoirs of the American Museum of Natural Historyy
Amer. Natur.	American Naturalist
Amer. Ophthalm. Soc. Trans.	Transactions of the American Ophthalmological Society
American Perfumer	American Perfumer and Essential Oil Review, The
Amer. Phil. Soc. Proc.	Proceedings of the American Philosophical Society held at Philadelphia
Amer. Phil. Soc. Trans.	Transactions of the American Philosophical Society, held at Philadelphia, for promoting useful knowledge
Amer. Phot.	American Photography
Amer. Poly. J	The American Polytechnic Journal
Amer. Quart. J. Agric.	American Quarterly Journal of Agriculture and Science
Amer. Reports State Entom.	See Ill., Mass, Mo., N. Y.
Amer. Soc. Agr. Sci. Proc.	Proceedings of the Society for the Promotion of Agricultural Science
Amer. Soc. Civ. Engin. Trans.	Transactions of the American Society of Civil Engineers
Amer. Soc. Micro Proc.	Proceedings of the American Society of Microscopists
Amer. Sugar. Ind	American Sugar Industry and Beet Sugar Gazette, The
Amer. Vet. Rev, N. Y.	American Veterinary Review, N. Y.
Amherst. Agric. Sta. Report	Annual Report of the State Agricultural Experiment Stations, at Amherst, Mass.
Amici, Giorn. Loscano	Giornale Loscano di Scienze medichi, fisiche e naturali
Amiens Acad. Sci. Mem.	Memoirs de l'Academie des Sciences, des Lettres et des Arts d'Amiens

Ammon, Monatschr. Med.	Monatschrift für Medecin, Augenheilkunde, und Chirurgie
Ammon, Zts. Opthalm.	*Zeitschrift für die Ophthalmologie*
Amsterdam	Werken van het Genootschap ter Bevordering der Natuur-, Geneesen Heelkunde. See Maandbl. Nat.
Amsterdam, Akad. Jaarb.	Jaarboek van de koningklijke Akademie van Wetenschappen gevestigd te Amsterdam
Amsterdam, Akad. Proc.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings of the Section of Sciences
Amsterdam, Akad. Verh.	Verhandelingen der koninklijke Akademie van Wetenschapp.
Amsterdam, Akad. Versl. Mededeel.	Verslagen en Mededeelingen der Koninklijke Akademie van Wetenschappen. Afdeeling Naturkunde
Amsterdam, Akad. Wet. Proc.	Processen-Verbaal van de gewone Vergaderingen der Koninklijke Akademie van Wetenschappen. Afdeeling Natuurkunde.
Amsterdam, Archief Wisk. Genoots	Archief uitgegeven door het Wiskundig Genootschap
Amsterdam Bijdr. Dierk.	Bijdragen tot de Dierkunde uitgegeven door the (Konincklijk Zoologisch) Genootschap Natura Artis Magistra, te Amsterdam
Amsterdam, Bull. Congr Bot.	Bulletin du Congres International de Botanique et d'Horticulture reuni a Amsterdam
Amsterdam Congr. Bot Actes	Actes du Congres International de Botanistes, d'Horticulteurs ....tenu a Amsterdam, en 1877
Amsterdam Genootsch. "Natura Artis Magistra"	See Amsterdam Bijdr. Dierk
Amsterdam Genootsch. Nat.-, Genees- en Heelkunde	See Maandbl. Nat.
Amsterdam, Het Inst.	Het Instituut
Amsterdam, Mengelwerk	Mengelwerk von uitgeleezene en andere Wisen Natuurkundige Verhandelingen
Amsterdam, Nieuw. Verh.	Nieuwe Verhandelingen der eerste Klasse van het Koninklijk Nederlandsche Instituut van Wetenschapen, en Schoone Kunsten te Amsterdam
Amsterdam, Nieuw. Wis. Voorstel.	Verzameling van nieuwe wiskundige Voorstellen door de Leden van het Wiskundig Genootschap, onder de zinspreuk: *Een onvermoeide arbeid komt alles te boven*, elkander tot onderlinge oefening opgegeven
Amsterdam Nederl. Aardr. Genootsch. Tijdschr.	Tijdschrift van het (Kon.) Nederlandsch. Aardrijkskundig Genootschap, gevestigd te Amsterdam
Amsterdam, Onderz. Phys. Lab.	Onderzoekingen gedaan in het Physiologisch Laboratorium van de Doorluchtige en Klinische Scholen te Amsterdam
Amsterdam, Tijdschr. Natuurk. Wetens.	Tijdschrift voor Natuurkundige Wetenschappen en Kunsten
Amsterdam, Tijdschr. Wis. Natuurk. Wetens.	Tijdschrift voor de Wis- en Natuurkundige Wetenschappen, Letterkunde, en Schoone Kunsten te Amsterdam
Amsterdam, Verh.	Verhandelingen der Eerste Klasse van het Koninklijk Nederlandsche Instituut van Wetenschappen, Letterkunde, en Schoone Kunsten te Amsterdam
Amsterdam, Verh. Genoots. Geneesk.	Verhandelingen van het Genootschap ter Bevordering der Geneesen Heilkunde, en Schoone Kunsten te Amsterdam
Amsterdam, Verzam. Ber. Navig.	Verzameling van Berichten over eenige onderwerpen der Navigatie

Amsterdam. Zool. Genoot-sch. "Natura Artis Magistra"	See Nederl. Tijdschr. Dierk
Anales agron.	Anales Agronomicos
Anales fis. quim.	Anales de la sociedad espanola de fisica y quimica
Anales inst. med. nacional	Anales del instituto medico nacional
Anales Mineria Mex	Anales de la Mineria Mexicana, Revista de Minas
Analyst	The Analyst, including the Proceedings of the Society of Public Analysts
Anat.	Anatomie
Anat. Anz	Anatomischer Anzeiger. Centralblatt fur die Gesamte Wissenschaftliche Anatomie. (Amtliches Organ der Anatomischen Gesellschaft)
Anat. Ges	See Anat. Anz.
Anat. Hefte	Anatomische Hefte. Referate und Beiträge (Beiträge und Referate) zur Anatomie und Entwickelungsgeschichte.
Anat. Soc. Proc.	See J. Anat. Physiol.
Anat. Studien	Anatomische Studien
Angers Acad. Sci. Mem	Memoires de l'Academie des Sciences et Belles-Lettres d'Angers
Angers, Ann. Soc. Linn	Annales de la Société Linneenne du departement de Maine et Loire
Angers, Mem. Soc. Agric.	Mémoires de la Société d'Agriculture, Sciences, et Arts
Angers, Soc Sci. Bull.	Bulletin de la Société d'Etudes Scientifiques d'Angers
Ann.	Liebig's Annalen der Chemie
Ann. Bot.	Annals of Botany
Ann. Chim.	Annales de Chimie
Ann. Chim. anal	Annales de Chimie analytique applique á l'Industrie, a l'Agriculture, á la Pharmacie et á la Biologie
Ann. chim farm.	Annali di Chimica e de farmacologia
Ann. Chim. Phys.	Annales de Chimie et de Physique
Ann Chimica	Annali di Chimica (Medico-Farmaceutica e di Farmacologia)
Ann. Conduct. Ponts et Chauss.	Annales des Conducteurs des Ponts et Chaussees et des Gardes-Mines
Ann. Conserv. Arts Met.	Annales du Conservatoire des Arts et Metiers
Ann. Dermatol.	Annales de Dermatologie et de Syphiligraphie
Ann. Ecole norm.	Annales scientifiques de l'Ecole Normale superieure (L. Pasteur)
Ann. Falsif.	Annales des Falsifications
Ann. Farm. Chim.	Annali di Farmacoterapia e Chimica (Biologica)
Ann. Fis. Chim.	Annali di Fisica, Chimica, etc.
Ann. Génie Civil	Annales du Génie Civil
Ann. Gén. Sci. Phys.	Annales générales des Sciences Physiques
Ann. Geogr.	Annales de Geographie
Ann. Hydrogr.	Annales Hydrographiques
Ann Hydrogr. Mar. Met.	Annalen der Hydrographie und Maritimen Meteorologie. Organ des Hydrographischen Bureaus (Amtes) und der Deutschen Seewarte
Ann. hyg pub.	Annales d'hygiene publique
Ann. Ind.	Annales industrielles, par Fredureau, etc.
Ann. Inst. Pastuer	Annales de l'Institut Pasteur
Ann. Landw.	Annalen der Landwirthschaft in den K. Staaten
Ann. Landw. Wochenbl.	Annalen der Landwirtschaft, Wochenblatt
Ann. Mag. Natur. Hist.	The Annals and Magazine of Natural History, including Zoology, Botany and Geology

Ann. Matemat.	Annali di Matematica pura ed applicata
Ann. Math.	Annals of Mathematics
Ann. Med.	Annali di Medicina
Ann. Med. Psychol.	Annales medico-psychologiques; Journal de l' anatomie, Physiologie, etc., du systeme nerveux
Ann. Med. Surg.	Annals of Medicine and Surgery, or Records of the occurring Improvements and Discoveries in Medicine, Surgery, and their immediately connected Arts and Sciences
Ann. Microgr.	Annales de Micrographie specialement consacrees a la Bacteriologie, aux Protophytes et aux Protozoaires
Ann. Mines	Annales des Mines. . .redigees et publiees sous l'Autorisation du Ministre des Travaux Publics
Ann. Museo Ind. Ital.	Annali del R. Museo Industriale Italiano
Ann. Natur. Hist.	Annals of Natural History
Ann. Oculist	Annales d'Oculistique et de Gynecologie
Ann. Pharm.	Annals of Pharmacy
Ann. Pharm. Louvain	Annales de Pharmacie, Louvain
Ann. Phil.	Annals of Philosophy
Ann. Phys.	Annalen der Physik
Ann. Phys. Chem.	Annalen der Physik und Chemie
Ann. Ponts et Chauss.	Annales des Ponts et Chausses
Ann. R. Staz. Chim.	Annali della R. Stazione Chimico Agraria Sperimentale di Roma
Ann. Rep., U. S. Dept. Agric.	Annual Report of the United States Department of Agriculture
Ann. sci. agron.	Annales de la science agronomique francaise et étrangére
Ann. Sci. Bot. Nat.	Annales des Sciences Naturelles, Botanique
Ann. Sci. Lomb. Veneto	Annali delle Scienze del Regno Lombardo-Veneto
Ann. Sci. Nat.	Annales des Sciences Naturelles. Botanique. Zoologie et Paleontologie, comprenant l'Anatomie, la Physiologie, la Classification et l'Histoirie Naturelle des Animaux
Ann. Sci Univ. Jassy	Annales scientifiques de l'Université de Jassy
Ann. Scott. Natur. Hist.	The Annals of Scottish Hatural History
Ann. Surg.	Annals of Surgery
Ann. Storia Natur.	Annali di Storia Naturale
Ann. Telegr.	Annales Telegraphiques
Annab.-Buchh. Ver. Naturk. Ber.	Bericht über den Annaberg-Buchholzer Verein fur Naturkunde
Annab.-Buchh. Ver. Naturk. Jahr	Jahresbericht des Annaberg-Buchholzer Vereins für Naturkunde
Annaes Sci. Natur.	Annaes de Sciencias Naturaes
Anneè Biol.	L'Anneè Biologique. Comptes Rendus annuers des Travuax de Biologie Generale
Annot. Zool. Jap.	Annotationes Zoologicae Japonenses, Auspiciis Societatis Zoologicae Tokyonensis seriatim editae
Annuaire Ancienne Normandie	Annuaire des cinq. Departements de l'Ancienne Normandie, par l'Association Normandie
Annuaire Inst. Provinces	Annuaire de l'Institut des Provinces, des Societes Savantes, et des Congres Scientifiques
Annuaire met. France	Annuaire Meteorologique de la France
Annuaire Mines Russie	Annuaire du Journal des Mines de Russie
Anthropol. (Paris)	Materiaux pour l'Histoire de l'Homme. Revue d'Anthropologie. Revue d'Ethnographie reunis.
Anthropol. Congr	See Congr. Int. Anthrop. C. R.
Anthropol. Inst. J.	The Journal of the Anthropological Institute of Great

Anthropol. Rev.	The Anthropological Review
Anthropol. Soc. Mem.	Memoirs read before the Anthropological Society of London
Antwerpen, Verh. Genoots. Occ. qui non.	Verhandelingen van het Genootschap. "Occidit qui non servat"
Anvers, Ann. Soc. Med.	Annales de la Societe de Medecine d'Anvers
Anvers, Congr. Sci. Geogr.	Compte-Rendu du Congres des Sciences Geographiques, Cosmographiques et Commerciales
Anvers, J. Pharm.	Journal de Pharmacie, publ par la Soc de Pharmacie d'Anvers
Apoth. Ztg.	Apotheker Zeitung, Berlin
Apothecary	Apothecary, Boston
Appreturzeitung	Appreturzeitung
Apt, Ann Soc Sci.	Annales de la Societe litteraire, scientifique et artistique d'Art (Vaucluse)
Aquila	Aquila. A Magyar Ornithologiai Kozpont Folyoirata. Periodical of Ornithology
Arb Kais. Gesundhts.	Arbeiten aus dem kaiserlichen Gesundheitsamte, Berlin
Arb pharm Inst., D. Univ. Berlin	Arbeiten aus dem pharmazeutischen Institut der Universität Berlin
Arcachon Soc. Sci. Stat. Zool. Trav	Société Scientifique et Station Zoologique d'Arcachon
Arcetri Oss Pubbl.	See Firenze R. Ist. Pubbl. (Arcetri Oss)
Archief Suikerind.	Archief Suikerindustrie in Nederlandsch-Indie
Archief Wisk. Genoots.	Archief uitgegeven door het Wiskundig Genootschap
Archit. and Eng.	Architect and Engineer
Archiv. Agriculturchem.	See Hermbstadt
Archiv. Anat. Micro.	Archives d'Anatomie Microscopique
Archiv. Anat. Physiol.	Archiv. fur Anatomie, Physiologie und wissenschaftliche Medicin
Archiv Anthropol.	Archiv. fur Anthropologie . Organ der deutschen Gesellschaft fur Anthropologie, Ethnologie und Urgeschichte
Archiv. Anthropol. Etnol.	Archivio per l'Anthropologia e la Etnologia
Archiv. Augenheilk.	Archiv. fur Augenheilkunde
Archiv. Augen- Ohrenheilk.	Archiv fur Augen- und Ohrenheilkunde
Archiv. belges méd. mil.	Archives belges de médicine militaire
Archiv. Biol.	Archives de Biologie
Archiv. Bot. Nord. France	Archives Botaniques du Nord de la France
Archiv. Chem. Mikros.	Archiv. Chemie und Mikroskopie
Archiv. Cosmol.	Archives cosmologiques. Revue des Sciences Naturelles, avec leurs applications a la Medecine, a l'Agriculture, aux Arts, et a l'Industrie
Archiv. Dent.	Archives of Dentistry: A record of Dental knowledge; medical, surgical, microscopical, chemical, and mechanical
Archiv. Elect.	Archives de l'Electricite
Archiv. Entwickl. Organ.	Archiv. fur Entwicklungsmechanik der Organismen
Archiv exper. Path. Pharm.	Archiv. für experimentelle Pathologie und Pharmakologie
Archiv. Farmacol. sper. Roma	Archivio di Farmacolagia sperimentale e Scienze affini. Roma
Archiv. fisiol.	Archivio di fisiologia
Archiv. gen. Med.	Archives generales de Medecine
Archiv. ges. Physiol.	Archiv. für die gesammte Physiologie des Menschen und der Thiere (Pfluger)
Archiv. Heilk.	Archiv der Heilkunde

Archiv. Hyg.	Archiv. für Hygiene
Archiv. Internal Med.	Archives of Internal Medicine
Archiv. intl. pharmacodyn	Archives internationales de pharmacodynamie et de thereapie
Archiv. Ital. Biol.	Archives Italiennes de Biologie. Revues, Résumés Reproductions des Travaux Scientifiques Italiens
Archiv. Kinderheilk	Archiv. fur Kinderheilkunde
Archiv. Math. Naturvid.	Archiv. for Mathematik og Naturvidenskab
Archiv. Math. Phys.	Archiv. der Mathematik und Physik
Archiv. Med.	Archives of Medicine
Archiv. Med. comparee.	See Rayer
Archiv. med. exp.	Archives de medicine experimentale et d'anatomie pathologique
Archiv. Med. Navale	Archives de Medecine Navale (et Coloniale)
Archiv. Med. Pharm Militair.	Archives de Medecine et de Pharmacie Militaires
Archiv. Mikro. Anat.	Archiv. fur Mikroskopische Anatomie (und Entwickelungsgeschichte)
Archiv. Miss. Sci.	Archives des Missions Scientifiques et Litteraires
Archiv. Naturgesch.	Archiv. fur Naturgeschichte
Archiv. Naturk. (Dorpat)	Archiv. fur die Naturkunde Liv-, Ehst- und Kurlands. Herausgegeben von der Dorpater Naturforscher-Gesellschaft
Archiv. Neerland.	Archives Neerlandaises des Sciences Exactes et Naturelles publiees par la Societe Hollandaise des Sciences a Harlem
Archiv. Ohrenheilk.	Archiv. fur Ohrenheilkunde
Archiv. Ophthalm.	Albrecht von Graefe's Archiv fur Ophthalmologie
Archiv. Ophthalm. Otol.	Archives of Opthalmology and Otology
Archiv. Otol.	Archives of Otology
Archiv. Parasit.	Archives de Parasitologie
Archiv. path. Anat.	Archiv fur pathologische Anatomie und Physiologie und fur klinische Medizin (Virchow's)
Archiv. Pharm.	Archiv. der Pharmacie; Archiv des Apothekervereins im nördlichen Deutschland.
Archiv. Pharm. og Chemi	Archiv. de Pharmaci og Chemi, Copenhagen
Archiv. Physiol.	Archives de Physiologie Normale et Pathologique
Archiv. Psychiatr.	Archiv. für Psychiatrie und Nervenkrankheiten
Archiv. Sci.	Archives of Science and Transactions of the Orleans County Society of Natural Sciences
Archiv. sci. med.	Archivio per les scienze mediche
Archiv. Sci. Phys. Nat.	Bibliotheque Universelle. Archives des Sciences Physiques et Naturelles
Archiv. Sci. Pract. Med.	Archives of Scientific and Practical Medicine
Archiv. Slaves Biol.	Archives Slaves de Biologie
Archiv. Verdauungs-krankh.	Archiv. fur Verdauungs-krankheiten
Archiv. Wiss. Heilk.	Archiv. des Vereins fur gemeinschaftliche Arbeiten zur Forderung der wissenschaftlichen Heilkunde
Archiv. Wiss. Prakt. Thierheilk.	Archiv. fur wissenschaftliche und praktische Thierheilkunde
Archiv. Zool. Anat. Fis.	Archivio per la Zoologia, l'Anatomia, e la Fisiologia
Archiv. Zool. Exper.	Archives de Zoologie Experimentale et Generale
Arcueil, Mem. Phys.	Memoires de Physique et de Chimie de la Societe d'Arcueil
Argent. Inst. Geogr. Bol.	Boletin del Instituto Geografico Argentino
Argent. P.	Argentine Patent
Argent. Soc. Ci. An.	Anales de la Sociedad Cientifica Argentina

Arkiv. Kemi, Minerol. Geol.	Arkiv for Kemi, Mineralogi och Geologi
Arkiv. Math. Astron. Fysik	Arkiv for Mathematik Astronomi och Fysik
Armagh Nat. Hist & Phil. Soc.	See Irish Natlist
Arms and Expl.	Arms and Explosives
Arnhem, Natuurk.	Natuurkunde Tijdschrift, inhoudende Phijsica, Chemie, Pharmacie, Natuurlijke Historie en Litteratuur, uitgegeven van wege het Genootschap *Tot nut en vergenoegen*, te Arnhem
Arras, Mem. Acad	Memoires de l'Academie d'Arras
Arras, Mem. Soc. Roy	Memoires de la Societe Royale d'Arras
Art. J.	The Art Journal
Artiz.	The Artizan (London)
Artus, Jahr. ökon Chemie	Jahrbuch fur okonomische Chemie, etc
Artus[illegible]rteljahresschrift	Vierteljahresschrift fur technische Chemie, Landwirthschaftliche Gewerbe, Fabrickwesen und Gewerbetreibende uberhaupt
Ashmol. Soc. Proc	Abstracts of the Proceedings of the Ashmolean Society
Asiat Researches	Asiatic Researches; or Transactions of the (Bengal) Society
Asiot. Soc. J.	Journal of the Royal Asiatic Society
Assoc. Franc. Compt rend	Association Francaise pour l'avancement des Sciences. Comptes Rendus
Assoc. Med. J	See Med. Assoc Journ.
Assur. Mag	The Assurance Magazine (and Journal of the Institute of Actuaries)
Astron Nachr.	Astronomische Nachrichten
Astron. Soc. Mem	Memoirs of the Astronomical Society of London
Astron. Soc. Month Not	Monthly Notices of the Astronomical Society of London
Astrophys J.	Astrophysical Journal
Atelier Phot.	Atelier des Photographen
Ateneo Ital.	L'Ateneo Italiano
Athenes Obs Nat Ann	Annales de l'Observatoire National d'Athenes
Atlantis	The Atlantis, or Register of Literature and Science
Atti. Accad Ital	Atti dell'Accademia Italiana di Scienze
Atti. accad. Lincei	Atti della reale accademia dei Lincei, rendiconti, classe di scienze fisiche, mathematiche e naturali
Atti. Coll. Ing. Archit	Atti de Collegio degli Ingegneri ed Architetti in Milano
Atti inst. incoragg.	Atti del R instituto d'incoraggiamento di Napoli, Naples, Italy
Atti R. Accad. Sci Torino	Atti della Reale Accademia della Scienze di Torino
Atti Sci Ital.	Riunione degli Scienziati Italiani
Atti Soc. Elvet.	Atti della Societa Elvetica delle Scienze Naturali
Aube, Mem. Soc. Agric.	Memoires de la Societe d'Agriculture des Sciences, e des Lettres du department de l'Aube
Augsb. Naturhist Ver. Ber.	Berichte des Naturhistorischen Vereins in Augsburg
Auk	The Auk A Quarterly Journal of Ornithology
Ausland	Das Ausland
Aust. P.	Austrian Patent
Aust.-Hung. P.	Austro-Hungarian Patent
Australasian Assoc. Rep.	Report of the . . Meeting of the Australasian Association for the Advancement of Science
Australasian J. Pharm.	Australasian Journal of Pharmacy, Melbourne
Australian Med. J.	Australian Medical Journal

Australia Med. Rec.	Medical Records of Australia
Australian P.	Australian P.
Australian Sugar J.	Australian Sugar Journal
Autun, Mem. Soc. Eduenne	Memoires de la Societe Eduenne
Auvergne, Ann. Sci.	Annales Scientifiques, Litteraires, et Industrielles de l'Auvergne
Auxerre, Bull. Soc. Sci.	Bulletin de la Societe des Sciences Historiques et Naturelles de l'Yonne
Badischen Aerzt. Verein. Mitth.	Mittheilungen des Badischen ärztlichen Vereins
Bah. P.	Bahamas Patent
Ballenstedt, Archiv.	Archiv fur die neuesten Entdeckungen aus der Urwelt
Ballot, Mag. Landbouw.	Magazin voor Landbouw en Kruidkunde
Baltimore Med. Phys Recorder	Baltimore Medical and Physical Recorder
Bamb. Naturf. Ges. Ber.	Bericht der naturforschenden Gesellschaft zu Bamberg
Barb. P.	Barbados Patent
Barcelona Acad. Bol.	Boletin de la Real Academia de Ciencias y Artes de Barcelona
Barcelona Acad. Mem.	Memorias de la Real Academia de Ciencias Naturales y Artes de Barcelona
Barrow Field Club Report	Barrow Naturalists' Field Club and Literary and Scientific Association. Annual Report and Proceedings
Basel, Ber	Bericht uber die Verhandlungen der Naturforschenden Gesellschaft in Basel
Batavia Genootsch Verh.	Verhandlingen van het Bataviaasch Genootschap der Kunsten en Wetenschappen
Batavia, Natuur. Archief.	Natuur- en Geneeskundig Archief voor Nederlandsch-Indië
Batavia, Natuurk. Tijdschr.	Natuurkundig Tijdschrift voor Nederlandsch-Indië, uitgegeven door de Koninklijke Natuurkundige Vereeniging in Nederlandsch-Indië
Batavia, Notulen	Notulen van de Allgemeene en Bestuurs-Vergaderingen van het Bataviaasch Genootschap van Kunsten en Wetenschappen
Batavia Obs. Obsns.	Observations made at the (Royal) Magnetical and Meteorological Observatory at Batavia
Batavia, Tijdschr.	Tijdschrift voor Indische Taal-, Land-, en Volkenkunde
Batavia, Verh. Natuurk. Vereen.	Verhandlingen der Natuurkundige Vereeniging in Nederlandsch-Indië
Bath Micro. Soc. Minutes	Extracts from the Minutes of the Bath Microscopical Society
Bath Natur. Hist. Club. Proc.	Proceedings of the Bath Natural History and Antiquarian Field Club
Bath Soc. Agric. Letters	Letters and Papers of the Bath and West of England Society for the Encouragement of Agriculture, Arts, Manufactures, and Commerce
Baugew. Ztg.	Baugewerks-Zeitung
Baumgartner Zts.	Zeitschrift fur Physik, Mathematik, und verwandte Wissenschaften
Bayer. Gewerbeztg.	Bayerische Gewerbezeitung
Bayer. Kunst. Gewerbebl.	Kunst und Gewerbeblatt (Poletechn. Verein Königreich Bayern)
Bayer, Landw. Ver. Erg.	Ergebnisse landwirthschaftlicher und agrikulturchemischer Versuche an der Station des General-Comite des Bayerischen Landwirthschaftlichen Vereines in München

Bayeux, Mem. Soc. Agric.	Memoires de la Societe d'Agriculture, Sciences, Arts, et Belles-Lettres de Bayeux
Bd. Trade J.	Board of Trade Journal
Beauvais, Soc. Acad. Mem.	Memoires de la Societe Academique d'Archeologie, Sciences et Arts du Department de l'Oise
Beitr. Anat. Physiol	See Eckhard
Beitr. Anthropol. Bayerns	Beitrage zur Anthropologie und Urgeschichte Bayerns. Organ der Munchener Gesellschaft für Anthropologie, Ethnologie und Urgeschichte
Beitr. Biol. Pflanz.	Beiträge zur Biologie der Pflanzen
Beitr. Geophys.	Beitrage zur Geophysik. Abhandlungen aus dem Geographischen Seminar der Universitat Strassburg. Beitrage zur Geophysik. Zeitschrift fur Physikalische Erdkunde
Beitr. Kryptog. Schweiz	Beitrage zur Kryptogamenflora der Schweiz
Beitr. Mecklenb. Aerzte	Beitrage Mecklenburgischer Aerzte zur Medicin und Chirurgie
Beitr. Morphol.	Beitrage zur Morphologie und Morphogenie. Untersuchungen aus dem Anatomischen Institut su Erlangen
Beitr. Naturk. Preussens	Beiträge zur Naturkunde Preussens. Herausgegeben von der Königlichen Physikalisch-Oekonomischen Gesellschaft zu Konigsberg
Beitr. Paläont. Oesterr.-Ung.	Beiträge zur Palaontologie Oesterreich-Ungarns und des Orients
Beitr. Path. Anat.	Beitrage zur Pathologischen Anatomie und Physiologie. Beirtäge zur Pathologischen Anatomie und zur Allgemeinen Pathologie
Beitr. Physiol. Morphol.	Beitrage zur Physiologie und Morphologie Niederer Organismen.
Beitr. Russ Reich.	Beiträge zur Kenntniss des Russischen Reiches und der angrenzenden Länder Asiens
Belfast, Clin. Soc. Trans.	Transactions of the Clinical and Pathological Society of Belfast
Belfast Field Club Rep.	Annual Reports and Proceedings of the Belfast Naturalists' Field Club
Belfast Natur. Hist. Soc. Proc.	Proceedings of the Belfast Natural History and Philosophical Society
Belg. Horticole	La Belgique Horticole. Annales de Botanique et d'Horticulture
Belg. P.	Belgian Patent
Bengal Asiat. Soc. J.	Journal of the Asiatic Society of Bengal
Bengal Asiat. Soc. Proc.	Proceedings of the Asiatic Society of Bengal
Bengal Govt. Records	Selections from the Records of the Bengal Government
Bengal, Phot. Soc. J.	Journal of the Photographic Society of Bengal
Ber.	Berichte der Deutschen Chemischen Gesellschaft, Berlin
Ber. deut. bot. Ges.	Berichte der deutschen botanischen Gesellschaft
Ber. pharm. Ges.	Berichte der deutschen pharmazeutischen Gesellschaft
Ber. phys. Ges.	Berichte der deutschen physikalischen Gesellschaft
Ber. Sächs. Ges. Wiss.	Berichte über die Verhandlungen der Konigl. Sachs. Gesellschaft der Wissenschaften zu Leipzig
Ber. Veter. König. Sach.	Berichte uber das Veterinarwesen im Konigreich Sachsen
Berg. Hüttenm. Jahr.	Berg- und hüttenmannisches Jahrbuch
Berg. Huttenm. Ztg.	Berg- und hüttenmannische Zeitung

Bergens Mus. Aarb.	Bergens Museums Aarbog for...Afhandlinger og Aarsberetning udgivne af Bergens Museum
Berggeist	Der Berggeist
Berghaus, Ann.	Annalen der Erd-, Völker- und Staatenkunde
Berghaus, Zts. Erdk.	Zeitschrift für vergleichende Erdkunde
Berlin Afrik. Ges. Mitth.	Mittheilungen der Afrikanischen Gesellschaft in Deutschland
Berlin Akad. Abh.	Abhandlungen der k. Akademie der Wissenschaften zu Berlin
Berlin Akad. Monatsber.	Monatsberichte der k. Preussischen Akademie der Wissenschaften zu Berlin
Berlin Akad. Sitzber.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin
Berlin Ann. Telegr.	Annalen der Telegraphie
Berlin Astron Jahr.	Berliner Astronomisches Jahrbuch
Berlin Bot. Gartens Jahr	Jahrbuch des Königlichen Botanischen Gartens und des Botanischen Museums zu Berlin
Berlin Bot. Gartens Notizbl.	Notizblatt des Königl. Botanischen Gartens und Museums zu Berlin
Berlin Ent. Ges.	See Ill. Wschr. Ent.
Berlin Entom. Zts.	Berliner Entomologische Zeitschrift; herausg. von dem Entomologischen Verein in Berlin
Berlin Ges. Anthrop. Verh	See Ztschr. Ethnol.
Berlin Ges. Erdk. Verh.	Verhandlungen der Gesellschaft fur Erdkunde zu Berlin
Berlin Ges. Erdk. Zts.	See Berlin Zts. Erdk.
Berlin Ges. Geburtshlf Gynäk.	See Zts. Geburtshlf. Gynäk.
Berlin Ges. Naturf. Freunde Mag.	Magazin der Gesellschaft Naturforschender Freunde zu Berlin, fur die neuesten Entdeckungen in der gesammten Naturkunde
Berlin Ges. Naturf. Freunde N. Schr.	Neue Schriften derGesellschaft Naturforschender Freunde in Berlin
Berlin Ges. Naturf. Freunde Verh.	Verhandlungen der Gesellschaft Naturforschender Freunde zu Berlin
Berlin Ges. Psychiatr.	See Arch. Psychiatr.
Berlin Gesundheitsamt Biol. Abth. Arb.	Arbeiten aus der Biologischen Abtheilung fur Land- und Forstwirthschaft am Kaiserlichen Gesundheitsamte
Berlin Ind. Ztg.	Industrie Zeitung, Berlin
Berlin Jahr. Pharm	Berlinisches Jahrbuch fur die Pharmacie und für die damit verbundenen Wissenschaften
Berlin Klin. Wochenschr.	Berliner klinische Wochenschrift
Berlin Mem. Acad.	Memoires de l'Academie Royale des Sciences de Berlin
Berlin Mitth. Ges. Naturf	Mittheilungen aus den Verhandlungen der Gesellschaft Naturforschender Freunde zu Berlin
Berlin Monatsber.	Monatsberichte der K. Preuss. Akademie der Wissenschaften zu Berlin
Berlin Monatsber. Ges. Erdk.	Monatsberichte uber die Verhandlungen der Gesellschaft für Erdkunde zu Berlin
Berlin Naturf. Freunde Sitzber.	Sitzungs-Berichte der Gesellschaft Naturforschender Freunde zu Berlin
Berlin Neue Zts. Geburtsk.	Neue Zeitschrift für Geburtskunde
Berlin Physiol. Ges. Verh.	See Arch. Anat. Physiol
Berlin Physik. Reichsanst. Abh.	Wissenschaftliche Abhandlungen der Physikalisch Technischen Reichsanstalt
Berlin Verh. Med. Ges.	Verhandlungen der Berliner medicinischen Gesellschaft

Berlin Zool. Mus. Mitth.	Mittheilungen aus der Zoologischen Sammlung des Museums für Naturkunde in Berlin
Berlin Zts. Erdk.	Zeitschrift der Gesellschaft für Erdkunde zu Berlin
Berlin Mitth.	Mittheilungen der Naturforschenden Gesellschaft in Bern
Berwick, Natur. Club Hist.	History of the Berwickshire Naturalists' Club
Berz. Jahr. Chem.	Berzelius Jahresberichte der Chemie
Besancon, Mem. Soc. Emul.	Memoires et Comptes Rendus de la Societe (Libre) d'Émulation du Doubs
Besancon, Seances Publ.	Seances publiques de l'Academie des Sciences, Arts, et Belles-Lettres de Besancon
Beton Eisen	Beton und Eisen
Betterave	Betterave
Beziers Soc. Sci. Bull.	Bulletin de la Société d'Etude des Sciences Naturelles de Beziers
Bianconi Rep. Ital.	Repertorio Italiano Per la Storia Naturale
Bibl. Anat.	Bibliographie Anatomique. Revue des Travaux en langue francaise. Anatomie. Histologie. Embryoologie. Anthropologie
Bibl. Bot.	Bibliotheca Botanica. Abhandlungen aus dem Gesammtgebiete der Botanik
Bibl. Brit.	Bibliotheque Britannique, ou Recueil extrait des Ouvrages Anglais periodiques et autres; partie des Sciences et Arts
Bibl. Ital.	Giornale dell' I. R. Istituto Lomgardo di Scienze, Lettere ed Arti, e *Biblioteca Italiana*
Bibl Math.	Bibliotheca Mathematica. Zeitschrift fur Geschichte der Mathematik. Journal d'Histoire des Mathematiques. Bibliotheca Mathematica. Zeitschrift für Geschichte der mathematischen Wissenschaften
Bibl. Univ.	Bibliotheque Universelle des Sciences, Archives des Sciences Physiques et Naturelles
Bibl. Zool.	Bibliotheca Zoologica
Bied. Zentr.	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb
Bierbrauer	Der Bierbrauer
Bijdr. tot de Dierkunde	Bijdragen tot de Dierkunde
Biochem. Bull.	Biochemical Bulletin
Biochem. J.	The Bio-Chemical Journal
Biochem. Zentr.	Biochemisches Zentralblatt, Leipzig
Biochem. Zts.	Biochemische Zeitschrift
Biol. Bull.	Biological Bulletin
Biol. Zentr.	Biologisches Zentralblatt
Biophys. Zentr.	Biophysikalisches Zentralblatt, Leipzig
Birmingham Natur. Hist. & Micro. Soc. Trans.	See Midland Natlist Trans.
Birmingham Phil. Soc. Proc.	Proceedings of the Birmingham Philosophical Society
Blankenburg, Ber.	Berichte des Naturwissenschaftlichen Vereins des Harzes zu Blankenburg
Blätter Blech-Arb.	Deutsche Blätter für Blecharbeiter
Blätter Kunstgew.	Blätter für Kunstgewerbe
Blätter Zuckerrüb.	Blätter für Zuckerrübenbau
Bleekrode, Nieuw Tijdschrift	Nieuw Tijdschrift gewijd aan alle takken van Volksvlijt, Nijverheid, Landbouw, Mijnwezen, Handel, Spoorwegen, Telegraphie en Scheepvaart
Blois, Mem. Soc. Sci.	Memoires de la Société des Sciences et des Lettres de Blois
Blois, Soc. Loir et Cher Mem.	Memoires de la Société des Sciences et Lettres de Loir et Cher

Boerhaave	Boerhaave
Böhm. Ges. Abh.	Abhandlungen der Königlich Böhmischen Gesellschaft der Wissenschaften
Böhm. Ges. Wiss. Jahr.	Jahresbericht der königl. böhm. Gesellschaft der Wissenschaften
Böhm. Monatschr. Ges. Mus.	Monatschrift des Gesellschaft des Vaterländischen Museums in Böhmen
Bol. P.	Bolivia Patent
Boll. chim. farm.	Bolletino chimico farmaceutico, Milan
Boll. estac. agr. Ciudad Juarez	Boletin de la estacion agricola experimental de Ciudad Juarez
Boll. ingen.	Boletin de ingenieros
Boll. Natur. Siena	Bollettino del Naturalista Collettore, Allevatore, Coltivatore
Bologna Accad. Sci. Mem.	Memorie della (R.) Accademi delle Scienze dell' Istituto di Bologna
Bologna, Mem. Inst. Naz. Ital.	Memorie dell'Istituto Nazionale Italiano
Bologna, Mem. Soc. Med.	Memorie della Societa Medica di Bologna
Bologna, Mem. Soc. Med. Chir.	Memorie della Societa Medico-chirurgica di Bologna
Bologna, Nov. Comment.	Novi Commentarii Academiae Scientiarum Instituti Bononiensis
Bologna, Opusc.	Opuscoli della Societa Medico-chirurgica di Bologna
Bologna, Opusc. Sci.	Opuscoli Scientifici
Bologna, Opusc. Sci. N. Coll.	Nuova collezione d'Opuscoli Scientifici
Bologna Rend.	Rendiconto delle Sessioni dell' Accademia Reale delle Scienze dell' Istituto di Bologna
Bombay, Agric. Hort. Soc. Proc.	Proceedings of the Agricultural and Horticultural Society of Western India
Bombay Govt. Records	Selections from the Records of the Bombay Government
Bombay, Med. Phys. Soc. Trans.	Transactions of the Medical and Physical Society of Bombay
Bombay Natur. Hist. Soc. J.	The Journal of the Bombay Natural History Society
Bombay, Roy. Asiat. Soc. J.	The Journal of the Bombay Branch of the Royal Asiatic Society
Bone, Acad. Hippone Bull.	Bulletin de l'Academie d'Hippone
Bonn, Corresp. Blatt Nat. Hist. Ver.	Correspondenzblatt des Naturhistorischen Vereins für Rheinland und Westphalen
Bonn, Niederrhein. Ges. Sitzber.	Sitzungsberichte der Niederrheinischen Gesellschaft für Natur- und Heilkunde zu Bonn
Bonn, Untersuch. Physiol. Lab.	Untersuchungen aus dem physiologischen Laboratorium zu Bonn
Bonn, Verh. Naturhist. Ver.	Verhandlungen des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens
Bonplandia	Bonplandia
Bordeaux, Acad. Sci. Seances Publ.	Seances publiques de l'Academie Royale des Sciences, Belles-Lettres, et Arts de Bordeaux
Bordeaux, Actes Acad. Sci.	Recueil des Actes de l'Academie des Sciences, Belles-Lettres, et Arts de Bordeaux
Bordeaux, J. Med.	Journal de Medecine de Bordeaux
Bordeaux, J. Med. Prat.	Journal de Medecine pratique, ou Recueil des Travaux de la Société de Medecine de Bordeaux
Bordeaux, Mem. Soc. Med. Chir.	Memoires et Bulletins de la Société Medico-Chirurgicale des Hopitaux et Hospices de Bordeaux
Bordeaux, Mem. Soc. Sci. Phys	Memoires de la Société des Sciences Physiques et Naturelles de Bordeaux

Bordeaux, Soc. Linn. Actes	Actes de la Société Linneenne de Bordeaux
Bordeaux, Soc Linn. Bull.	Bulletin d'Histoire Naturelle de la Société Linneenne Bordeaux
Bordeaux, Soc. Med. Mem.	Memoires et Bulletins de la Société de Medecine et de Chirurgie de Bordeaux
Bordeaux, Soc. Sci. P.-V.	Proces-Verbaux des Seances de la Société des Sciences Physiques et Naturelles de Bordeaux
Bornemann, Der Ingenieur	Der Ingenieur
Boston J. Phil.	The Boston Journal of Philosophy and the Arts
Boston J. Natur. Hist.	Boston Journal of Natural History
Boston Med. Surg. J.	Boston Medical and Surgical Journal
Boston, Mem Amer. Acad.	Memoirs of the American Acedemy of Arts and Sciences
Boston, Mem. Natur. Hist. Soc.	Memoirs read before the Boston Society of Natural History
Boston Pap. Soc. Natur. Hist.	Occasional papers of the Boston Society of Natural History
Boston, Proc. Natur. Hist. Soc.	Proceedings of the Boston Society of Natural History
Boston Soc. Med. Sci J.	Journal of the Boston Society of Medical Sciences
Bot. Centr.	Botanisches Centralblatt. Referirendes Organ für das Gesammtgebiet der Botanik des In- und Auslandes
Bot. Centr. Beihefte	Beihefte zum Botanischen Centralblatt
Bot. Cong. Proc.	The International Horticultural Exhibition and Botanical Congress· Report of Proceedings
Bot. Gaz.	The Botanical Gazette
Bot. Jahr. (Engler)	Botanische Jahrbucher, Engler, Leipzig
Bot. Mag , Tokyo	The Botanical Magazine, Tokyo
Bot. Notiser	Botaniska Notiser
Bot Tidsskr.	Botanisk Tidsskrift udgivet af den Botaniske Forening i Kjobenhavn
Bot. Untersuch.	Botanische Untersuchungen aus dem Physiologischen Laboratorium der landwirthschaftlichen Lehranstalt in Berlin
Bot. Untersuch. (Brefeld's)	Untersuchungen aus dem Gesammtgebiete der Mykologie
Bot. Ver. Gesamtthüringen	See Jena Geogr. Ges. Mitth.
Botan. Ztg.	Botanische Zeitung
Bot. Zentr.	Botanisches Zentralblatt
Botaniste	Le Botaniste
Bouchardat, Archiv.	Archives de Physiologie, de Therapeutique, et d'Hygiene
Boue, J. Geol.	Journal de Geologie
Boulogne, Mem. Soc. Agric.	Memoires de la Société d'Agriculture, etc., de Boulogne-sur-Mer
Bourse cuirs Liege	Bourse aux cuirs de Liege, bulletin hebdomadaire
Brandenb. Bot. Ver. Verh.	Verhandlungen des botanischen Vereins fur die Provinz Brandenburg
Brass World	Brass World and Platers Guide, The
Braunk.	Braunkohle
Braunschw. Ver. Naturwiss. Jahr.	Jahresbericht des Vereins für Naturwissenschaft zu Braunschweig
Braz. P.	Brazilian Patent
Bremen Abh.	Abhandlungen herausgegeben vom Naturwissenschaftlichen Verein zu Bremen
Brenn. Ztg.	Brennerei Zeitung
Brera, Giorn. Med. Prat.	Giornale di Medicina Pratica
Brera, Nuovi Comment.	Nuovi Commentari di Medicina

Brescia, Comment. Ateneo	Commentarj della Accademia di Scienze, Lettre, ed dell'Ateneo di Brescia
Breslau, Ann. Klin. Inst.	Annalen des Klinisch-chirurgischen Instituts auf der Universität zu Breslau
Breslau, Bot. Garten Arb.	Arbeiten aus dem Konigl. Botanischen Garten zu Breslau
Breslau, Gewerbebl.	Breslauer Gewerbeblatt
Breslau, Jahr. Schles Ver. Berg.	Jahrbuch des Schlesischen Vereins für Berg- und Huttenwesen
Breslau, Schles. Ges. *Jahr.*	*Jahresbericht des Akademischen Naturwissenschaftlichen Vereins zu Breslau*
Breslau, Studien Physiol. Inst.	Studien des Physiologischen Instituts zu Breslau
Breslau, Zts Klin. Med.	Zeitschrift fur Klinische Medicin
Brest Soc Acad Bull.	Bulletin de la Société Academique de Brest
Brewers J. (Lon.)	Brewers Journal and Hop and Malt Trades Review The (London)
Brewers J., N. Y.	Brewers Journal, New York
Brick	Brick
Brick J.	Brick, Pottery and Glass Journal
Brick and Clay Record	Brick and Clay Record
Brighton, Proc. Natur. Hist. Soc.	Reports and Abstracts of the Proceedings of the Brighton and Sussex Natural History Society
Bristol Proc. Nat. Soc.	Proceedings of the Bristol Naturalists' Society
Brit. Assoc. Rep.	Report of the Meetings of the British Association for the Advancement of Science
Brit. Clay Worker	British Clay Worker, The
Brit. Food J.	British Food Journal
Brit. For. Med. Chir. Rev.	British and foreign Medico-Chirurgical Review
Brit. Inst Publ Health	See J. State Med.
Brit. J. Almanac	British Journal of Photography Almanac
British J. Dent Sci.	The British Journal of Dental Science
Brit. J. Phot.	British Journal of Photography
Brit. Med. J.	British Medical Journal
Brit. Mycol. Soc. Trans.	The British Mycological Society Transactions
Brit. Pharm. Confer. Proc.	Proceedings of the British Pharmaceutical Conference
Brit. Pharm. Confer Trans.	Year Book of Pharmacy, comprizing Abstracts of Papers. With the Transactions of the British Pharmaceutical Conference
Brit. Colon. Drug.	British and Colonial Druggist, London
Brit. Guiana Agr. Soc.	See Timehri
Brit Guiana P.	British Guiana Patent
Brit. Hond. P.	British Honduras Patent
Brooklyn Entom. Soc. Bull.	Bulletin of the Brooklyn Entomological Society
Brosche, Zts.	Zeitschrift fur Natur- und Heilkunde
Broussais, Ann.	Annales des la Medicine Physiologique
Brown Sequard, J. Physiol.	Journal de la Physiologie de l'Homme et des Animaux
Brugnatelli, Giorn.	Giornale di Fisica, Chimica, e Storia Naturale
Brunn Verh.	Verhandlungen des Naturforschenden Vereines in Brünn
Brux. Acad. Bull.	Bulletins de l'Academie Royale des Sciences, etc., de Belgique
Brux. Acad. Cent. Anniv.	Centieme Anniversaire de Foundation de l'Academie Royale de Belgique
Brux. Acad. Med. Belg. Bull	Bulletin de l'Academie Royale de Medecine Belgique
Brux. Acad. Sci. Mem.	Nouveaux memoires de l'Academie Royale, des Sciences et Belles-lettres de Bruxelles

Brux. Actes Soc. Med.	Actes de la Société Medicale de Bruxelles
Brux. Ann. Soc. Entom. Belge	Annales de la Société Entomologique Belge
Brux. Ann. Soc. Malacol.	Annales de la Société Malacologique de Belgique
Brux. Ann. Trav. Pub.	Annales des Travaux Publics de Belgique
Brux. Ann. Univ. Belg.	Annales des Universites de Belgique
Brux. Bull. Belge Phot.	Bulletin Belge de la Photographie
Brux. Bull. Soc. Bot.	Bulletins de la Société Royale de Botanique de *Belgique*
Brux. Congr. Bot. Act.	Actes du Congres de Botanique horticole reuni a Bruxelles
Brux. Congr. Bot. (C. R.)	Congres de Botanique et d'Horticulture de 1880 tenu a Bruxelles
Brux. J. Med.	Journal de Medecine, de Chirurgie, et de Pharmacologie
Brux. J. Soc. Centr. Agric.	Journal de la Société Centrale d'Agriculture de Belgique
Brux. Mem. Couronn.	Memoires Couronnes et Memoires des Savants Entrangers
Brux. Mus. Congo Ann.	Etat Independant du Congo. Annales du Musee du Congo, publiees par ordre du Secretaire d'Etat
Brux. Mus. Hist. Natur. Ann.	Annales du Musee Royal d'Historie Naturelle de Belgique
Brux. Mus. Hist. Natur. Bull.	Bulletin du Musee Royal d'Histoire Naturelle de Belgique
Brux. Mus. Hist. Natur. Mem.	Memoires du Musee Royal d'Histoire Naturelle de Belgique
Brux. Soc. Agric. Journ.	Journal de la Société Centrale d'Agriculture de Belgique
Brux. Soc. Belge Micro Ann.	Annales de la Société Belge de Microscopie
Brux. Soc. Belge Micro. Bull.	Bulletin (des Seances) de la Société Belge de Microscopie
Brux. Soc. Entom. Ann.	Annales de la Société Entomologique de Belgique
Brux. Soc. Entom. Mem.	Memoires de la Société Entomologique de Belgique
Brux. Soc. Linn. Bull.	Bulletin de la Société Linneenne de Bruxelles
Brux. Soc. Sci.	See Rev. Quest. Sci.
Brux. Soc. Sci. Ann.	Annales de la Société Scientifique de Bruxelles
Bucarest. Acad. Rom Anal.	Analele Academiei Romane
Bucarest Soc. Sci. Bul.	Buletinul Societatii de Sciinte (Fizice, Fixica, Chimia si Mineralogia) din Bucuresci-Romania. Bulletin de la Société des Sciences, Bucarest-Roumanie
Buchholz	See Annab.-Buchh. Ver. Nat. Jber.
Buda, Evkönyvei	A' Magyar Tudos Tarsasag' Evkonyvei (Year Books of the Hungarian Scientific Association)
Buda, Palyamunkak.	Termeszettudomanyi Palyamunkak
Buda, Tudomanytar.	Tudomanytar Közre bocsatja a' Magyar Tudos Tarsasag
Buffalo Bull.	Bulletin of the Buffalo Society of Natural Sciences
Builder	The Builder
Buitenzorg Inst. Bot. Bull.	's Lands Plantentuin. Bulletin de l'Institut Botanique de Buitenzorg
Buitenzorg Jard. Bot Ann.	Annales du Jardin Botanique de Buitenzorg
Bull. Acad. Med.	Bulletin of the Academy of Medicine
Bull. Acad. roy. Belg.	Academie royale de Belgique; Bulletin de la Classes des Sciences
Bull. Acad. Sci., Cracow.	Bulletin international de l'Academie des Sciences de Cracovie

Bull. Acad. Sci., Petrograd	Bulletin de l'Academie Imperiale des Sciences de Petrograd
Bull. Amer. Inst. Min. Eng.	*Bulletin American Institute of Mining Engineers*
Bull. Amer. Pharm. Assoc.	Bulletin of the American Pharmaceutical Association
Bull. assoc. chim. sucr. dist.	Bulletin de l'association des chemists de sucrerie distillerie de France
Bull. Bur. Agric.	Bulletin of the Bureau of Agricultural Intelligence and of Plant Diseases
Bull. Bur. Chem. U. S. Dept. Agric.	Bulletins, Bureau of Chemistry, U. S. Department of Agriculture
Bull. Bur. Mines	Bureau of Mines Bulletin, Department of the Interior
Bull. Bur. Standards	Bulletin of the Bureau of Standards
Bull. Col. School Mines	Bulletin of the Colorado School of Mines
Bull. Dept. Agric. Jamaica	Bulletin of the Department of Agriculture, Jamaica
Bull. Dept. Agric. Trinidad	Bulletin of Agricultural Information, Department of Agriculture, Trinidad
Bull. Geol. Inst. Univ. Upsala	Bulletin of the Geological Institute of the University of Upsala
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America
Bull. Hyg. Lab.	Bulletins of the Hygienic Laboratory, United States Public Health and Marine Hospital Service
Bull. Imp. Inst.	Bulletin of the Imperial Institute, London
Bull. Iron Assoc.	Bulletin of the American Iron and Steel Association
Bull. Johns Hopkins Hosp.	Bulletin of Johns Hopkins Hospital
Bull. Mass. Inst. Tech.	Bulletin of the Massachusetts Institute of Technology
Bull. Med. Belge.	Bulletin Medical Belge.
Bull. Musee	Bulletin du Musee de l'industrielle de Belgique
Bull. Pharmacie	Bulletin de Pharmacie
Bull. Pharmacy	Bulletin of Pharmacy
Bull. Pharm. Sud-est	Bulletin de Pharmacie du Sud-est, Montpellier
Bull. Sci. France Belg.	Bulletin Scientifique de la France et de la Belgique
Bull. Sci. Nord	Bulletin Scientifique, Historique et Litteraire du Department du Nord et des pays voisins
Bull. Sci. pharmacolog.	Bulletin des Sciences pharmacologiques
Bull. Soc. Bot. France	Bulletin de la Société Botanique de France
Bull. Soc. Bot. Belg.	Bulletin de la Société Royale de Botanique de Belgique
Bull. Soc. Chim.	Bulletin de la Société Chimique de France
Bull. Soc. Chim. Belg.	Bulletin de la Société Chimique de Belgique
Bull. Soc. Encourag.	Bulletin de la Société d'Encouragement
Bull. Soc. franc. Mineral.	Bulletin de la Société Francaise de Mineralogie
Bull. Soc. franc. Phot.	Bulletin de la Société Francaise de Photographie
Bull. Soc. geol. France	Bulletin de la Société geologique de France
Bull. Soc. Ind. Amiens	Bulletin de la société industrielle d'Amiens
Bull. Soc. Ind. Marseille	Bulletin de la Société industrielle de Marseille
Bull. Soc. Ind. Minerale	Bulletin de la société de l'industrie minerale
Bull. Soc. Ind. Mulh.	Bulletin de la société industrielle de Mulhouse
Bull. Soc. Ind. Nord	Bulletin mensuel de la société industrielle du Nord
Bull. Soc. Ind. Rouen	Bulletin de la société industrielle de Rouen
Bull Soc. internatl. elect.	Bulletin de la Société internationale des electriciens
Bull. Soc. Med. Amiens	Bulletin des Travaux de la Société Medicale d'Amiens
Bull. Soc. med. Gand	Bulletin de la Société de Medecine de Gand
Bull. Soc. Mycol.	Bulletin de la Société Mycologique de France
Bull. Soc. pharm. Bord.	Bulletin de la société pharmacie de Bordeaux
Bull. Soc. phot. Belg.	Bulletin de la Société photographique de Belgique
Bull. Soc. Romane Stiin.	Buletinul societatii Romane de Stiinte
Bull. Soc. roy. pharm.	Bulletin de la société de pharmacie de Bruxelles royale
Bull. Soc. sci. med. Rennes	Bulletin de la société scientifique et medicale de l'ouest, Rennes

Bull. Soc. vaudoise	Bulletin de la Société vaudoise des Ingenieurs et des Architects
Bull. Torrey Bot. Club	Bulletin of the Torrey Botanical Club, New York
Bull. Vulc. Ital.	Bullettino del Vulcanismo Italiano (e di Geodinamica generale)
C. A.	Chemical Abstracts
Cabanis, J. Ornithol.	Journal fur Ornithologie
Cadiz, Period. Mens. Cien	Periodico mensual de Ciencias matematicas y fisicas
Caen, Acad. Mem.	Memoires de l'Academie des Sciences, Belles Lettres, et Arts de Caen
Caen, Bull. Soc. Linn. Normandie	Bulletin de la Société Linneene de Normandie
Caen, Mem. Soc. Linn. Normandie	Memoires de la Société Linneenne de Normandie
Caen, Travaux	Precis des Travaux de la Société d'Agriculture, &c. de Caen
Calcutta, J. Natur. Hist.	The Calcutta Journal of Natural History
Calcutta, Quart. J.	Quarterly Journal of the Medico-Physical Society
Calcutta Roy. Bot. Gard. Ann.	Annals of the Royal Botanic Garden, Calcutta
Calcutta, Trans. Med. Phys. Soc.	Transactions of the Medical and Physical Society of Calcutta
Cal. Acad. Bull.	Bulletin of the California Academy of Sciences
Cal. Acad. Mem.	Memoirs of the California Academy of Sciences
Cal. Acad. Natur. Sci. Proc.	Proceedings of the Californian Academy of Natural Sciences
Cal. Acad. Pap.	Occasional Papers of the California Academy of Sciences
Cal. Min. Bur. Bull.	California State Mining Bureau. Bulletin
Cal. Min. Bur. Rep.	(California State Mining Bureau). Report of the State Mineralogist
Calvados, Mem Soc. Linn.	Memoires de la Société Linneenne du Calvados
Cambrai, Mem. Soc. Emul.	Memoires de la Société d'Emulation de Cambrai
Cambridge Mem. Analyt. Soc.	Memoirs of the Cambridge Analytical Society
Cambridge Mus Comp. Zool. Bull	Proceedings of the Museum of Comparative Zoology at Harvard College, Cambridge, Mass.
Cambr. Ornith. Club Bull.	Bulletin of the Nuttall Ornithological Club. A Quarterly Journal of Ornithology
Cambridge Phil Soc. Proc.	Proceedings of the Cambridge Philosophical Society
Cambridge Phil. Soc. Trans.	Transactions of the Cambridge Philosophical Society
Cambridge, Studies Physiol. Labor	Studies from the Physiological Laboratory in the University of Cambridge
Camera Oscura	La Camera Oscura; rivista periodica universale dei progressi della Fotografia
Can.	Canadian—Canada
Can., Bot. Soc. Ann.	Annals of the Botanical Society of Canada
Can. Chem. J.	The Canadian Chemical Journal
Can. Drug.	Canadian Druggist
Can. Eng.	Canadian Engineer, The
Can. Entom.	The Canadian Entomologist
Can. Entom. Soc. Rep.	First Annual Report on the Noxious Insects of the Province of Ontario
Can. Inst. Proc.	Proceedings of the Canadian Institute (Toronto, being a continuation of "The Canadian Journal of Science, Literature and History")
Can. Inst. Trans.	Transactions of the Canadian Institute
Can. J.	The Canadian Journal of Industry, Science, and Art

Can Naturalist	The Canadian Naturalist and Geologist, and Porceedings of the Natural History Society of Montreal
Can. P.	Canadian Patent
Can. Pat. Off. Rec.	Canadian Patent Office Record
Can Pharm J.	Canadian Pharmaceutical Journal and Pharmacal Gazette
Can Rec Sci.	The Canadian Record of Science, including the Proceedings of the Natural History Society of Montreal, and replacing the Canadian Naturalist
Can Roy. Soc. Proc. Trans.	Proceedings and Transactions of the Royal Society of Canada
Canestrini	See Archivio Zool.
Canestrini, Archiv.	Archivio per la Zoologia, l'Anatomia, e la Fisiologia
Cannes Soc. Mem.	Memoires de la Société des Sciences Naturelles (et Historiques), des Lettres et des Beaux-Arts de Cannes, et de l'arrondissement de Grasse
Cantu, Cronaca	Cronaca
Caout. Gutta-p.	Caoutchouc et la Gutta-percha
Caradoc Field Club Trans.	Transactions of the Caradoc and Severn Valley Field Club
Cardiff Natur Soc. Trans.	Cardiff Naturalists' Society. Report and Transactions
Carinthia	See Karnten
Carl, Rep. Physik.	Repertorium für Experimental-Physik., etc. (Rep der Physik)
Carlsberg Lab.	See under Kiobenh.
Carlsruhe	See Karlsruhe
Carlsruhe, Verh. Naturwiss. Ver.	Verhandlungen des Naturwissenschaftlichen Vereins
Carloinisches Medico-Chirurgisches Institut.	See under Stockh. Physiol. Lab. Mitth.
Carus, Zool. Anzeiger	Zoologischer Anzieger
Casopis	Casopis pro Pestovani Mathematiky a Fysiky. (Journal for the Advancement of Mathematics and Physica)
Casopis Cesketho Lekarn.	Casopis Cesketho Lekarnitura
Casper Vierteljahrssch.	Vierteljahrsschrift fur gerichtliche und öffentliche Medicin
Casper Wochensch.	Wochenschrift für die gesammte Heilkunde
Cassel Jahr.	Jahresbericht, dann Bericht, uber die Thatigkeit des Vereins fur Naturkunde in Cassel
Cassier's Mag.	Cassiers's Magazine
Castings	Castings
Catania Atti Accad. Gioen.	Atti dell'Accademia Gioenia di Scienze Naturali di Catania
Catania Boll. Accad. Gioen.	Bollettino delle Sedute della Accademia Gioenia
Cattaneo Bibl. di Farm.	Biblioteca di Farmacia, Chimica, etc.
Cattaneo Giorn Farm.	Giornale di Farmacia
Cell. Ind.	Die Celluloid Industrie
Cellule	La cellule
Cement	Cement
Cement Age	Cement Age
Cement Eng. News	Cement and Engineering News
Cement Record	Cement Record
Centr. Agrik. Chem.	Central-Blatt für Agrikulturchemie und rationellen Wirthschafts-Betrieb. Referirendes Organ für naturwissenschaftliche Forschungen in ihrer Anwendung auf die Landwirthschaft
Centr. Allg. Path.	Centralblatt für allgemeine Pathologie

Centr. Bakt.	Centralblatt für Bacteriologie und Parasitenkunde
Centr. Med. Wiss.	Centralblatt für die medicinischen Wissenschaften
Centr. Mineral.	Centralblatt fur Mineralogie, Geologie und Palaeontologie
Centr. Papierfabr.	Centralblatt für Papierfabrikation
Centr. Path.	Centralblatt für Allgemeine Pathologie und Pathologische Anatomie
Centr. Physiol.	Centralblatt fur Physiologie
Centr. Text. Ind	Centralblatt fur die Textil-Industrie
Centr. Zuckerind	Centralblatt fur die Zuckerindustrie
Centrztg. Optik	Central-Zeitung fur Optik und Mechanik (Elektrotechnik und verwandte Berufszweige)
Ceramique	Ceramique, La
Cette Stat. Maritime	See Montpellier Inst Zool. Trav
Cey. P.	Ceylon Patent
Chamb. Comm J.	Chamber of Commerce Journal
Chambery Mem. Acad. Savoie.	Memoires de la Societe Academique de Savoie
Charente-Inf. Soc Sci. Ann	Academie de la Rochelle Societe des Sciences Naturelles de la Charente-Inferieure Annales
Charkoff.	See Kharkov.
Charleston Med. Journ	Charleston Medical Journal and Review
Charleston South J. Med.	The Southern Journal of Medicine
Chem. Age	Chemical Age
Chem. Centr	Chemisches Centralblatt (1830-1906).
Chem. Coll. Reports	Reports of the Royal College of Chemistry, and Researches conducted in the Laboratories
Chem. Drug	Chemist and Druggist, London
Chem. Drug. Australasia	Chemist and Druggist of Australasia
Chem. Eng.	Chemical Engineer
Chem Gaz.	Chemical Gazette, The
Chem. Ind.	Chemische Industrie
Chem. Listy	Chemicke Listy
Chem News	Chemical News
Chem. Pharm Centr Blatt.	Chemisch-pharmaceutisches Central-Blatt
Chem. Rev	The Chemical Review
Chem. Rev. Fett-Harz-Ind.	Chemische Revue uber die Fett-und Harz-Industrie
Chem. Tech. Mitth.	Elsner's Chemisch-Technische Mittheilungen
Chem. Tech. Rep.	Chemisch-Technisches Repertorium (Jacobsen 1862-1901)
Chem. Tech. Neuzeit	Chemische Technologie der Neuzeit
Chem. Tech. Übers.	Chemisch-Technische Übersicht (supplement to Chem Ztg.)
Chem. Tech. Ztg.	Chemiker-und Techniker-Zeitung
Chem. Trade J.	Chemical Trade Journal and Chemical Engineer
Chem. Weekbl	Chemisch Weekblad
Chem. World	Chemical World, The
Chem. Zentr.	Chemisches Zentralblatt (1907-)
Chem. Ztg.	Chemiker-Zeitung
Chem. Ztg. Rep.	Repertorium der Chemiker Zeitung
Chem. Zts.	Chemische Zeitschrift
Chemist	The Chemist
Chemnitz Ber.	Bericht der Naturwissenschaftlichen Gesellschaft zu Chemnitz
Cherbourg Mem. Soc Acad.	Memoires de la Société Academique de Cherbourg
Cherbourg, Mem. Soc. Sci	Memoires de la Société Imperiale des Science Naturelles de Cherbourg

Cherbourg Soc. Sci. Natl. Mem.	Memoires de la Société Nationale des Sciences Naturelles et Mathematiques de Cherbourg
Chester Soc. Sci. Proc.	Proceedings of the Chester Society of Natural Science (and Literature)
Chicago Acad Sci. Bull	Bulletin of the Chicago Academy of Sciences
Chicago Acad. Sci. Bull Nat. Hist. Surv	The Chicago Academy of Sciences. Bulletin.. of the Natural History Survey
Chicago Acad. Sci. Trans.	Transactions of the Chicago Academy of Sciences
Chicago Entom. Soc. Mem.	Occasional Memoirs of the Chicago Entomological Society
Chicago Field Columb. Mus. Publ.	Publications of the Field Columbian Museum
Chile, Anales Univ.	Anales de la Universidad de Chile
Chile P.	Chilean Patent
Chili Soc. Sci. Act.	Actes de la Société Scientifique du Chili (Actas de la Sociedad Cientifica de Chile)
Chim. et Ind.	Chimie et Industrie
Chimiste	Chimiste, Le
Christiania, Forh.	Forhandlinger i Videnskabs-Selskabet i Christiania
Christiania, Norsk Mag.	Norsk Magazin for Laegevidenskaben
Christiania Skr. (Math - Nat. Kl.)	Skrifter udgivne af Videnskabsselskabet i Christiania. Mathematisk-naturvidenskabelig Klasse
Christiania, Univers. Lab.	Das chemische Laboratorium der Universitat Christiania
Chron. ind.	Chronique de l'industrie
Chur, Jahresber. Naturf. Gesell.	Jahresbericht der Naturforschenden Gesellschaft von Graubundten in Chur
Ciment	Ciment, Le
Cincin. Soc. Natur. Hist. Jl.	The Journal of the Cincinnati Society of Natural History
Cistula Entom	Cistula Entomologica
Civil Eng. Inst. Trans.	Transactions of the Institution of Civil Engineers
Civil Eng. J.	The Civil Engineer and Architect's Journal, etc.
Civilingenieur	Der Civilingenieur
Clay Worker	Clay Worker, The
Clermont, Mem. Acad. Sci.	Memoires de l'Academie des Sciences, Belles Lettres, Arts de Clermont-Ferrand
Cleveland Med. J.	Cleveland Medical Journal
Clin. Soc. Trans.	Transactions of the Clinical Society of London
Coblentz, Jahr. bot. Ver.	Jahresbericht des botanischen Vereines am Mitten und Niederrheine, mit botanischen Abhandlungen
Cohn, Beitr. Biol. Pflanz.	Beitrage zur Biologie der Pflanzen
Coimbra, Inst.	O Instituto; journal scientifico et letterario
Coimbra, Soc. Broter. Bol.	Sociedade Broteriana. Boletim Anual
Col. P.	Colombian Patent
Collegium	Collegium (Scientific technical supplement to Ledermarkt)
Colliery Guardian,	Colliery Guardian and Journal of the Iron and Coal Trades
Colmar Soc. Hist. Natur. Bull.	Bulletin de la Société d'Histoire Naturelle de Colmar
Colombia, Contrib.	Contribuciones de Colombia a las Ciencias i a las Artes
Colombo	See Ceylon
Colorado Sci. Soc. Proc.	Proceedings of the Colorado Scientific Society
Comment. Fauna &c. Ven. Trent.	Commentario della Fauna, Flora e Gea del Veneto e Trentino
Compt. rend.	Comptes rendus hebdomadaires des Seances de l'Academie des Sciences

Compt rend. Assoc Franc.	Association Francaise pour l'Avancement des Sciences. Compte Rendu de la 1^{e} (-12^{e}) Session; 1872–83
Compt. rend minerale	Comptes rendus de la Société de l'industrie minerale
Compt. rend Soc. biol.	Comptes rendus des seances et memoires de la Société de biologie, Paris
Compt. rend. trav. lab Carlsberg	Comptes rendus du travaux du laboratoire de Carlsberg
Concrete	Concrete
Concrete Age	Concrete Age
Concrete Constr. Eng.	Concrete and Constructional Engineering
Concrete Eng.	Concrete Engineering (no longer published separately. Combined with Cement Age)
Conegliano Scuola Vit. Enol Ann.	Annali della R. Scuola di Viticoltura e di Enologia in Conegliano
Conegliano Scuola Vit. Enol. N. Rassegna	Nuova Rassegna di Viticoltura de Enologia della R. Scuola di Conegliano
Conegliano Scuola Vit. Enol Riv	La Rivista Periodico (quindicinale, Organo) della R Scuola di Viticoltura e di Enologia (e del Comizio Agrario) di Conegliano
Cong P	Congo Free State Patent
Congr Anthropol Compt. Rend	Congres international d'Anthropologie et d'Archeologie prehistoriques Comptes Rendus
Congr. Bot. Crittog Atti	Societa Crittogamologica Italiana. Atti del Congresso Nazionale di Botanica Crittogamica in Parma
Congr. Bot Int. Atti	Atti del Congresso Internazionale di Genova
Congr. Int. Bot Bull.	Bulletin du Congres International de Botanique et d'Horticulture reuni a St Petersbourg .
Congr. Internatl. Hortic. Bull	Bulletin du Congres International d'Horticulture a Bruxelles
Congr. Internatl. Med. Atti	Atti dell' XI. Congresso Medico Internazionale
Congr. Internatl. Med C. R.	Comptes-Rendus du XII Congres International de Medecine
Congr Internatl Sci Med C. R.	Congres Periodique International des Sciences Medicales. Compte-Rendu
Congr. Internatl. Zool. (C. R.)	Congres International de Zoologie
Connecticut, Acad Mem	Memoirs of the Connecticut Academy of Arts and Sciences
Connecticut Acad. Trans.	Transactions of the Connecticut Academy of Arts and Sciences
Contrib. Biol. Veg.	Contribuzioni alla Biologia Vegetale
Copenhagen	See Kjobenhavn.
Copenhagen	See Congr Int. Sci. Med. C. R, 1884
Copenhague, Résumé	Résumé du Bulletin de la Société Royale Danoise des Sciences
Cordoba, Acad. Bol.	Boletin de la Academia Nacional de Ciencias Exactas existente en la Universidad de Cordoba
Cordoba Acad. Ci. Act.	Actas de la Academia Nacional de Ciencias en Cordoba
Corn Trade J.	Corn Trade Journal
Cornwall, J. Roy. Inst.	Journal of the Royal Institution of Cornwall
Cornwall Poly. Soc. Rep.	Royal Cornwall Polytechnic Society, Annual Report
Cornwall, Poly. Soc. Trans.	Reports and Transactions of the Royal Geological Society of Cornwall
Corresp. Blatt. Schweiz. Aerzte	Correspondenz-Blatt fur Schweizer Aerzte
Corresp. Blatt Zahn.	Correspondenzblatt für Zahnarzte
Cosmos	Cosmos· Revue Encyclopedique hebdomadaire

Costa, Corrisp. Zool.	Corrispondenza Zoologica, destinata a diffondere nel regno delle Due Sicilie tutto cio che si va discuoprendo entro e fuori Europa (e vice-versa), risguardante la Zoologia in generale
Cotteswold Club Proc.	*Proceedings of the Cotteswold Naturalists' Field* Club
Cracovie Acad. Sci. Bull	Bulletin International de l'Academie des Sciences de Cracovie
Cracow	See Krakow
Crell. Ann.	Chemische Annalen fur die Freunde der Naturlehre, etc.
Crichton, Russ. Sammlung	Russische Sammlung fur Naturwissenschaft und Heilkunst
Cron. med mex.	Cronica medica mexicana, Mexico
Croydon Micro Club Proc.	Proceedings and Transactions of the Croydon Microscopical and Natural History Club
Croydon Micro Club Rep.	Report and Abstract of Proceedings of the Croydon Microscopical (and Natural History) Club
Cuba P	Cuban Patent
Cuba, Rep Fis Nat.	Repertorio fisico naturale de la isla de Cuba
Cuir	Cuir, Le
Cumberland Assoc. Trans	Transactions of the Cumberland and Westmorland Association for the Advancement of Literature and Science
Cuyper, Rev. Univ.	Revue Universelle des Mines, de la Metallurgie, &c.
D'Alton u. Burm. Ztg Zool.	Zeitung fur Zoologie, Zootomie, und Palaeozoologie
Dan Biol Stat. Rep.	Report of the Danish Biological Station to the Home Department (Board of Agriculture)
Dan P.	Danish Patent
Danzig, Neu. Schrift	Neueste Schriften der Naturforschenden Gesellschaft in Danzig
Danzig, Schrift.	Schriften der Naturforschenden Gesellschaft in Danzig
Darmst. Beitr. Geol.	Beitrage zur Geologie des Grossherzogthums Hessen und der angrenzenden Gegenden
Darmst Ver. Erdk. Notiz.	Notizblatt des Vereins fur Erdkunde zu Darmstadt und des Mittelrheinischen Geologischen Vereins
Davenport Acad Proc.	Proceedings of the Davenport Academy of Natural Sciences
Dax Soc Borda Bull.	(Bulletin de la) Société de Borda, Dax (Landes)
Delft Ecole Poly. Ann.	Annales de l'Ecole Polytechnique de Delft
Delhi, Med. J.	Quarterly Medical and Surgical Journal for the North-West Provinces
Denison Univ. Sci. Lab. Bull	Bulletin of (the Scientific Laboratories of) Denison University
Dent. Cosmos	Dental Cosmos, Philadelphia
Dent Digest	The Dental Digest, Chicago
Dent. Rev.	The Dental Review
Deut. Amer Apoth. Ztg.	Deutsch-Amerikanische Apotheker Zeitung, New York
Deut. Amer. Gewerbeztg.	Illustrierte Deutsch-Amerikanische Gewerbe und Industrie-Zeitung (Newark, N. J.)
Deut Arch. Klin. Med.	Deutsches Archiv. fur Klinische Medizin
Deut. Bot. Ges. Ber.	Berichte der Deutschen Botanischen Gesellschaft
Deut. Bot. Monats.	Deutsche Botanische Monatsschrift
Deut. Buchdr. Ztg	Deutsche Buchdruker-Zeitung
Deut. Eisenbahn Ztg.	Zeitung des Vereins Deutscher Eisenbahn-Verwaltungen
Deut. Elektro. Ges.	See Zts. Elektroch.

Deut. Entom Zts.	Deutsche Entomologische Zeitschrift (formerly *Berliner Entomologische Zeitschrift*)
Deut. Geol. Ges. Zts.	Zeitschrift der Deutschen Geologischen Gesellschaft
Deut. Gerber Ztg.	Deutsche Gerber Zeitung
Deut. Ind. Ztg.	Deutsche Industrie Zeitung
Deut. Klinik	Deutsche Klinik
Deut. Mechan Ztg	Deutsche Mechaniker-Zeitung
Deut. med. Wochenschr.	Deutsche medizinische Wochenschrift
Deut. Monats	Deutsche Monatshefte
Deut. Naturf. Ber.	Amtlicher Bericht der...Versammlung Deutscher Naturforscher und Aerzte
Deut. Naturf. Festschr.	Festschrift für die 59 Versammlung Deutscher Naturforscher und Aerzte
Deut Naturf. Tagebl.	Tageblatt der. Versammlung Deutscher Naturforscher und Aerzte
Deut. Naturf. Versamml. Ber.	Bericht uber die Versammlung der Deutschen Naturforscher und Aerzte
Deut. Poly. Ztg.	Allgemeine Deutsche Polytechnische Zeitung (H. Grothe)
Deut. Phys. Ges. Verh	Verhandlungen der Deutschen Physikalischen Gesellschaft
Deut. Tech. Ztg	Deutsche Techniker Zeitung
Deut. Topfer Ziegl. Ztg.	Deutsche Topfer und Ziegler Zeitung
Deut Vierteljahrschr. Oeff. Gesundh.	Deutsche Vierteljahrsschrift fur Gesundheitspflege
Deut. Zool. Ges.	See Zool Anz.
Deut. Zool. Ges. Verh	Verhandlungen der Deutschen Zoologischen Gesellschaft
Deut. Zts Chirurg.	Deutsche Zeitschrift fur Chirurgie
Deut. Zts. Thiermed	Deutsche Zeitschrift fur Thiermedicin und vergleichende Pathologie
Deut. Zuckerind	Deutsche Zuckerindustrie
Devon Assoc. Trans.	Transactions of the Devonshire Association for the Advancement of Science, Literature and Art
Devon & Cornwall Natur Hist. Soc.	See Plymouth Inst. Trans.
Diamant Ztg	Diamant, Glas-Industrie Zeitung
Dietet. Hyg Gaz.	Dietetic and Hygienic Gazette, The
Dijon, Acad Sci. Mem	Memoires de l'Academie des Sciences, Arts et Belles-Lettres de Dijon
Dijon, J. Agric.	Journal d'Agriculture de la Cote d'Or
Dijon, Seances Acad.	Seances publiques de l'Academie des Sciences, Arts, et Belles-Lettres de Dijon
Dinant, Soc. Natur Bull.	Bulletin de la Société des Naturalistes Dinantais
Dingl. Poly.	Dinglers Polytechnisches Journal
Donders, Archiv	Archiv fur die Hollandischen Beitrage zur Natur- und Heilkunde
Dorpat, Archiv	Archiv fur die Naturkunde Liv-, Esth-, und Kurlands
Dorpat, Biol. Naturk.	Biologische Naturkind.
Dorpat, Naturf. Ges.	See Arch. Nat. (Dorpat)
Dorpat, Naturwiss. Abh.	Naturwissenschaftliche Abhandlungen aus Dorpat
Dorpat Pharm. Inst. Arb.	Arbeiten des Pharmakologischen Institutes zu Dorpat
Dorpat Sitzber.	Sitzungsberichte der Naturforscher-Gesellschaft bei der Universität (Jurjew) Dorpat
Dorpat Schr.	Schriften herausgegeben von der Naturforscher Gesellschaft bei der Universität (Jurjew) Dorpat
Dorset Field Club Proc.	Proceedings of the Dorset Natural History and Antiquarian Field Club

Douai Mem. Soc. Agric.	Memoires de la Société d'Agriculture, de Sciences, et d'Arts, seant a Douai
Doubs Soc Emul Mem	Memoires de la Société d'Emulation du Departement du Doubs
Dove Rep. Physik.	Repertorium der Physik. Enthaltend eine vollstandige Zusammenstellung der neuern Fortschritte dieser Wissenschaft
Dresden Ausz. Protokol	Auszuge aus den Protokollen der Gesellschaft für Natur- und Heilkunde in Dresden
Dresden Denkschr. Naturwiss Ges.-Isis.	Denkschriften der Naturwissenschaftlichen Gesellschaft Isis zu Dresden
Dresden Entom. Ver "Iris" Corresp.-Bl.	See Iris
Dresden Isis Festschr.	Festschrift der Naturwissenschaftlichen Gesellschaft Isis in Dresden
Dresden Isis Sitzber.	Sitzungsberichte und Abhandlungen der Naturwissenschaftlichen Gesellschaft Isis in Dresden
Dresden, Jahr. Natur. Heilk.	Jahresberichte fur 1858-60 v. d. Gesellschaft für Natur- und Heilkunde in Dresden
Dresden, Mitth. Poly. Schule	Mittheilungen der K. Sachs Polytechnischen Schule
Dresden, Schr. Ges. Mineral.	Auswahl aus den Schriften der unter Werner's Mitwirkung gestifteten Gesellschaft fur Mineralogie
Dresden, Sitzber Natur Heilk.	Sitzungsberichte der Gesellschaft fur Natur- und Heilkunde
D. R. P.	German Patent (Deutsches Reichs-Patent)
Drug. Circ.	Druggist's Circular
Drug Topics	Drug Topics, New York
Dublin, Geol. Soc J.	Journal of the Geological Society of Dublin
Dublin, Hosp Gaz.	Dublin Hospital Gazette
Dublin J. Med. Chem. Sci	Dublin Journal of Medical and Chemical Science
Dublin J. Med Sci.	The Dublin Journal of Medical Science
Dublin Med. Trans	Dublin Medical Transactions
Dublin Micro. Club	See Irish Natur
Dublin, Natur. Hist. Soc. Proc.	Proceedings of the Natural History Society of Dublin
Dublin Natur Field Club	See Irish Natur.
Dublin, Pathol Soc Proc.	Proceedings of the Pathological Society of Dublin
Dublin Quart. J.	The Dublin Quarterly Journal of Science
Dublin Quart. J. Med.	Dublin Quarterly Journal of Medical Science
Dublin, Roy. Soc J.	Journal of the Royal Dublin Society
Dublin Soc. J , Dublin Soc. Trans.	Transactions and Journal of the Dublin Society
Dublin Soc. Sci. Proc.	The Scientific Proceedings of the Royal Dublin Society
Dublin Soc. Sci. Trans.	The Scientific Transactions of the Royal Dublin Society
Dublin, Zool. Bot. Assoc. Proc.	Proceedings of the Dublin University Zoological and Botanical Association
Dudley, Geol. Soc. Proc.	Transactions of the Dudley and Midland Geological and Scientific Society
Dumfr. Gallow. Soc. Trans.	The Transactions and Journal of Proceedings of the Dumfriesshire and Galloway Natural History and Antiquarian Society
Dunkerque, Mem. Soc. Encour.	Memoires de la Société Dunkerquoise pour l'Encouragement des Sciences, des Lettres, et des Arts
Durham Univ. Phil. Soc. Proc.	Proceedings of the University of Durham Philosophical Society

Dyer, Calico Ptr.	Dyer, Calico Printer, Bleacher, Finisher, and Textile Review
Dzondi, Aeskulap	Aeskulap
Eastbourne Natur. Hist. Soc. Papers (& Trans.)	Papers (Transactions) of the Eastbourne Natural History Society
Eastbourne Natur. Hist. Soc. Proc.	The Sixth Annual Report of the Eastbourne Natural History Society
Eastbourne Natur. Hist. Soc. Trans.	Transactions of the Eastbourne Natural History Society
Echange	l'Echange Organe (Mensuel) des Naturalistes de la Region Lyonnaise
Eckhard, Beitr.	Beitrage zur Anatomie und Physiologie
Eclairage Elect.	l'Eclairage Electrique. Revue (hebdomadaire) d(el)'Electricite
Eclect. Med. J., Cincin	Eclectic Medical Journal, Cincinnati
Econ. Geol.	Economic Geology
Ecu. P.	Ecuador Patent
Edinb. Bot. Soc. Proc.	Proceedings of the Botanical Society of Edinburgh for the years 1855-56
Edinb. Bot. Soc. Trans	Transactions of the Botanical Society of Edinburgh
Edinb. Field Club Trans.	Transactions of the Edinburgh Naturalists' Field Club
Edinb., Fish Bd Rep.	Annual Report of the Fishery Board for Scotland
Edinb. J Med. Sci.	Edinburgh Journal of Medical Science
Edinb. J. Natur. Geogr. Sci.	The Edinburgh Journal of Natural and Geographical Science
Edinb. J. Sci.	The Edinburgh Journal of Science
Edinb. Med. Chir. Soc. Trans.	Transactions of the Medico-Chirurgical Society of Edinburgh
Edin Med. J.	Edinburgh Medical Journal
Edinb. Mem Wern Soc	Memoirs of the Wernerian Natural History Society
Edinb Monthly J. Med. Sci.	Edinburgh Monthly Journal of Medical Science
Edinb. Natur. Soc Trans.	Transactions of the Edinburgh Field Naturalists' and Microscopical Society, instituted as the Edinburgh Naturalists' Field Club
Edinb N Phil. J.	The Edinburgh New Philosophical Journal
Edinb Phil J.	The Edinburgh Philosophical Journal
Edinb Plin. Soc Trans.	Transactions of the Plinian Society
Edinb Proc. Phys. Soc.	Proceedings of the Royal Physical Society of Edinburgh
Edinb. Roy. Coll. Physns. Lab. Rep.	Reports from the Laboratory of the Royal College of Physicians, Edinburgh
Edinb. Roy. Soc. Proc.	Proceedings of the Royal Society of Edinburgh
Edinb Roy. Soc. Trans.	Transactions of the Royal Society of Edinburgh
Edinb. Trans. Scot. Soc Arts	Transactions of the Royal Scottish Society of Arts
Eisen Ztg.	Eisen Zeitung
Ekaterinburg	See Iekaterinenb.
Elberfeld Naturwiss, Ver. Jahr.	Jahres-Bericht des Naturwissenschaftlichen Vereins in Elberfeld
Elec. Rev.	The Electrical Review
Elec. Soc. Trans.	The Transactions and Proceedings of the London Electrical Society
Elec. Telegr. Rev.	The Electric Telegraph Review
Elec. World	Electrical World
Electrician	The Electrician
Electricite	l'Electricite
Electrochem. Met. Ind.	Electrochemical and Metallurgical Industry

Elektrochem Zts.	*Elektrochemische Zeitschrift*
Elektrotech Zts.	Electrotechnische Zeitschrift
Elliott Soc. J.	Journal of the Elliott Society of Natural History
Elliott Soc Proc.	Proceedings of the Elliott Society of Natural History
Elsner, Mitth.	See Chem.-Tech. Mitth.
Emden Naturf. Ges Jahr.	.. Jahresbericht der Naturforschenden Gesellschaft in Emden
Emden Naturf. Ges Schr.	Kleine Schriften der Naturforschenden Gesellschaft in Emden
Eng.	Engineering
Eng Contr	Engineering and Contracting
Eng. Digest	Engineering Digest
Eng Mag.	Engineering Magazine, The
Eng Mining J. (Eng Min J.)	Engineering and Mining Journal, The
Eng News	Engineering News
Eng Record	Enginering Record, Building Record and Sanitary Engineer
Engineer	Engineer, The
Engineers' J.	The Engineers' Journal and Railway Gazette of India and the Colonies
Engineers Soc Trans	Society of Engineers. Transactions
Engl Mech.	English Mechanic
Engler, Bot. Jahr.	Botanische Jahrbucher für Systematik, Pflanzengeschichte und Pflanzengeographie
Engrais, L'	Engrais, L'
Entom Annual	The Entomologist's Annual
Entom. Mag.	The Entomological Magazine
Entom Medd (Kjobenh)	Entomologiske Meddelelser udgivne af Entomologisk Forening
Entom Month Mag.	The Entomologist's Monthly Magazine
Entom Nachr	Entomologische Nachrichten
Entom. Record	The Entomologist's Record and Journal of Variation
Entom. Soc. Trans	The Transactions of the Entomological Society of London
Entom Tidskr.	Entomologisk Tidskrift pa Foranstaltande af Entomologiska Foreningen i Stockholm
Entomologica Amer.	Entomologica Americana
Entomologist	The Entomologist
E. P	English (British) Patent
Epicure	Epicure, The
Epidem Soc Trans.	Transactions of the Epidemiological Society of London
Epinal (Vosges) Ann.	Annales de la Société d'Emulation du departement des Vosges
Erdel Muz.-Egyl Ertek.	Az Erdelyi Muzeum-Egylet Kiadvanyai Ertekezesek. (Publications of the Transylvanian Museum Association. Memoirs)
Erdmann, Sveriges Geol. Undersok.	Sveriges geologiska Undersokning, pa offentlig bekostnad, utford under Ledning af A. Erdmann
Erfurt, Abh. Akad. Wiss.	Abhandlungen der Kurfürstlich Mainzer Akademie nützlicher Wissenschaften zu Erfurt
Erfurt, Akad. Jahr.	Jahrbucher der königlichen Akademie gemeinnütziger Wissenschaften zu Erfurt
Erfurt, Denkschr.	Denkschrift der Akademie gemeinnütziger Wissenschaften in Erfurt
Erfurt, Nova Acta	Nova Acta Academiae Electoralis Moguntinae

Ergeb. Physiol.	Ergebnisse der Physiologie, Wiesbaden
Erlangen, Abh.	Abhandlungen der Physikalisch-medicinischen Societat in Erlangen
Erlangen Anat. Inst.	See Bietr. Morphol
Erlangen, Mitth. Phys. Med. Soc.	Wissenschaftliche Mittheilungen der Physikalisch-medicinischen Societät zu Erlangen
Erlangen Phys. Med. Soc. Sitzber.	Sitzungsberichte der Physikalisch Medizinischen Societat zu (in) Erlangen
Erythea	Erythea A Journal of Botany, West American and General
Essex Field Club Proc.	Journal of Proceedings of the Essex Field Club
Essex Field Club Spec Mem.	Essex Field Club Special Memoirs
Essex Field Club Trans	Transactions of the Essex Field Club
Essex Inst Bull.	Bulletin of the Essex Institute
Essex Inst Commun	Communications read before the Essex Institute
Essex Inst Proc.	Proceedings of the Essex Institute
Essex Natur. Hist Soc J	Journal of the Essex County Natural History Society
Essex Natlist.	The Essex Naturalist
Essig Ind.	Deutsche Essigindustrie
Etudes Gites Mineraux	See France Gites Min Etudes
Eure, Bull. Acad. Ebroic	Bulletin de l'Academie Ebroicienne
Eure, J. Agric.	Journal d'Agriculture, de Medicine et des Sciences accessoires
Eure, Recueil Trav.	Recueil des Travaux de la Société Libre d'Agriculture, des Sciences, des Arts et des Belles-Lettres du departmente de l'Eure
Eure, Soc Agric. Bull.	Bulletin de la Société d'Agriculture, des Sciences, et des Arts du departement de l'Eure
Eure, Soc Agric Recueil	Recueil de la Société d'Agriculture, Sciences, Arts, et Belles Lettres du departement de l'Eurs
Evkonyv	A' Magyar Tudos Tarsasag' Evkonyvei
Exner Rep.	Repertorium der Physik.
Exper. Sta Rec	Experiment Station Record
Eyr	Eyr, et Medicinsk Tidsskrift
Fachgenosse	Fachgenosse, Der
Falaise, Mem. Soc. Acad	Memoires de la Société Academique des Sciences, &c , de Falaise
Farben Ztg.	Farben Zeitung
Farb. Ztg.	Farber Zeitung (Lehne's)
Fechner Centr	Centralblatt fur Naturwissenschaften und Anthropologie
Fechner, Rep.	Repertorium der Experimental-Physik
Fed. Inst. Min. Engin. Trans.	Transactions of the Federated Institution of Mining Engineers
Fer.	Ferrum, Halle
Ferussac, Bull. Sci. Math.	Bulletin des Sciences Mathematiques, Astronomiques, Physiques, et Chimiques par le Baron de Ferussac
Ferussac, Bull. Sci. Natur.	Bulletin des Sciences Naturelles et de Geologie
Feuille Jeunes Natur.	Feuille des Jeunes Naturalistes
Field Mus. Natur. Hist.	Field Museum of Natural History, Chicago, Publication
Fij. P.	Fiji Islands Patent
Fin. P.	Finland Patent
Finistere Soc. Sci. Bull.	Bulletin de la Société d'Etudes Scientifiques du Finistere
Finlande Soc. Geogr.	See Fennia
Finska Läk. Sällsk. Handl.	Finska Låkare Sallskapets Handlingar
Finska Vet.-Soc.	See Helsingfors, Bidrag. Helsingfors, Öfvers

Firenze Accad. Georgofili Atti	Atti della Reale Accademia Economico-Agraria dei Georgofili di Firenze
Firenze, Ann. Mus Fis	Annali del R. Museo di Fisica e Storia Naturale
Firenze, Ann. Mus Imp.	Annali del Museo Imperiale di Fisica e Storia Naturale di Firenze
Firenze Congr Bot Atti	Atti del Congresso Internazionale Botanico tenuto in Firenze nel mese di Maggio 1874
Firenze, Mem. Soc Ital.	See Modena
Firenze, Opusc. Sci	Collezione d'Opuscoli scientifici.
Firenze R. Inst. Pubbl.	Pubblicazioni del R. Istituto di Studi Superiori Pratici e di Perfezionamento in Firenze
Firenze Soc. Georgofili Atti	Atti della (Real) Societa Economica di Firenze ossia de' Georgofili
Firenze Soc. Studi Geogr. Boll.	See Riv. Geogr. Ital.
Flora	Flora oder Allgemeine Botanische Zeitung
Flore Jardins	Annales d'Horticulture et de Botanique, ou Flore des Jardins du Royaume des Pays-Bas
Flore Serres	Flore des Serres et des Jardins de l'Europe
Florence	See Firenze
Florke, Repert	Repertorium des neuesten und wissenwurdigsten aus der gesammten Naturkunde
Foldt Kozlon	Foldtani Kozlony, Havi folyoirat kiadja a Magyarhoni Foldtani Tarsulat
Folia Clin	Folia clinica chimico et microscopica
Folia haematol.	Folia haematologica
Folia Therap. Lond.	Folia Therapeutica, London
Forbes, Med. Rev.	The British and Foreign Medical Review, or Quarterly Journal of Practical Medicine and Surgery
Forsch. Agr -Phys.	Forschungen auf dem Gebiete der Agrikultur-Physik.
Forster, Allg Bauztg.	Allgemeine Bauzeitung
Fortschr. Chem.	Fortschritte der Chemie, Physik und Physikalischen chemie
Fortschr Med.	Fortschritte der Medicin
Fortschr. Phys.	Die Fortschritte der Physik.
Fortschr. Rontgenstr.	Fortschritte auf dem Gebiete der Rontgenstrahlen
Fortschr. Theerfarben-Fabrikation	Fortschritte der Theerfarbenfabrikation und verwendter Industriezweige
Foundry	Foundry, The
F. P.	French Patent
France, Congr. Med. Chir.	Congres Medico-Chirurgicale de France
France, Congr. Sci.	Sessions des Congres Scientifiques de France
France Gites Miner Etudes	Etudes des Gites Mineraux de la France
France, Inst. Provinces Annuaire	Annuaire de l'Institut des Provinces et des Congres Scientifiques de France
France, Inst. Provinces Mem.	Memoires de l'Institut des Provinces de France: Sciences physiques et naturelles
France Soc. Agric. Bull.	Bulletin des Seances de la Société Nationale d'Agriculture de France
France Soc. Agric. Mem.	Memoires publies par la Société Nationale d'Agriculture de France
France Soc. Bot. Bull.	Bulletin de la Société Botanique de France
France Soc. Entom.	See Abeille., Paris, Soc. Ent. Ann., Paris, Soc. Ent. Bull , Rev. Ent.
Franc Soc. Miner. Bull.	Bulletin de la Société Mineralogique de France. Bulletin de la Société Francaise de Mineralogie. (Ancienne Société Mineralogique de France)
France Soc. Zool.	See Paris, Caus. Sci.
France Soc. Zool. Bull.	Bulletin de la Société Zoologique de France

France Soc. Zool. Mem.	Memoires de la Société Zoologique de France
Frankfurt	See Senckenberg
Frankfurt, Jahr. Phys. Ver.	Jahrbuch zur Verbreitung naturwissenschaftlicher Kenntnisse, veranstaltet vom Physikalischen Verein zu Frankfurt a/Main
Frankf. Ver Pflege Phot.	See Wien, Photogr Correspond
Frankfurt, Zool Garten	Der Zoologische Garten Frankfurt a/M.
Frankfurter Zts. Pathol.	Frankfurter Zeitschrift fur Pathologie
Franzos. Ann.	Franzosische Annalen fur die allgemeine Naturgeschichte, Physik, &c
Freiberg, Jahr Berg. Hutt.	Jahrbuch fur den Berg- und Huttenmann. Herausg. von der Konigl. Berg-Akademie zu Freiberg
Freiburg, Beitr.	Beitrage zur Rheinischen Naturgeschichte
Freiburg, Ber.	Berichte uber die Verhandlungen der Naturforschenden Gesellschaft zu Freiburg i. B.
Freie K.	Freie Kunste
Frelon	Le Frelon Journal d'Entomologie descriptive
Fries, Bot Notiser	Botaniska Notiser
Froriep, Notizen	Notizen aus dem Gebiete der Natur- und Heilkunde
Fuhling's Ztg.	Fuhlings landwirtschaftliche Zeitung
Gac ind	La Gaceta industrial
Gand. Ann Soc. Agric	Annales de la Société Royale d'Agriculture et de Botanique
Gand, Ann Soc. Med.	Annales de la Société de Medecine de Gand
Gand, Bull Soc. Med.	Bulletin de la Société de Medecine de Gand
Gard, Apercu Trav.	Notice ou Apercu analytique des Travaux de l'Academie Royale du Gard
Gard, Mem Acad.	Memoires de l'Academie du Gard
Gard, Notice Trav. Acad	Notice des Travaus del'Academie du Gard
Garden & Forest	Garden and Forest. A Journal of Horticulture, Landscape Art and Forestry
Gardeners Chron	The Gardeners Chronicle
Garnett, Ann Phil	Annals of Philosophy, Natural History, Chemistry &c.
Garten-Flora	Garten-Flora
Garten-Ztg.	Neue allgemeine Deutsche Garten- und Blumenzeitung
Gartenwelt	Gartenwelt, The
Gas World	Gas World, The
Gaz	Le Gaz
Gazz. del Clin	Gazzetta della Cliniche
Gazz. med. ital lomb.	Gazzetta medica italiana lombardia, Milano
Gazz. Chim. Ital.	Gazzetta Chimica Italiana
Geelong Field Natur. Club	See Wombat
Gehlen J.	Journal fur dei Chemie und Physik
Gendrin, Trans. Med.	Transactions Medicales
Geneeskundig Mag.	Geneeskundig Magazijn
Geneve, Archiv.	See Archives Sci. Phys Nat.
Geneve, Bull. Soc. Ornith Suisse.	Bulletin de la Societe Ornithologique Suisse
Geneve Conserv. Bot. Annuaire	Annuaire du Conservatoire du Jardin Botanique de Geneve
Geneve, Inst. Natl. Bull.	Bulletin de l'Institut National Genevois
Geneve. Inst. Natl. Mem.	Memoires de l'Institut National Genevois
Geneve, Mus. Hist. Natur. Ann.	See Rev. Suisse Zool.
Geneve, Recueil Trav Soc. Med.	Recueil des Travaux de la Société Medicale de Geneve
Geneve, Soc. Geogr. Mem.	Memoires de la Société de Geographie de Geneve

Geneve, Soc Phys Mem.	Memoires de la Société de Physique et d'Histoire Naturelle de Geneve
Genie civ.	Genie Civil
Genova	See Congr. Bot Int. Atti. 1892
Genova, Ann Mus Phys	Annali del Museo Civico di Storia Naturale
Genova, Giorn.	Giornale degli Studiosi di Lettere, Science, arti e Mestieri
Genova, Mem. Accad.	Memoire dell'Accademia Imperiale delle Scienze di Genova
Genova, Mem Ist. Ligure.	Memorie dell' Istituto Ligure
Genova, Mem. Soc. Med. Emul.	Memorie della Societa Medica di Emulazione di Genova
Genova Mus Civ. Ann.	Annali del Museo Civico di Storia Naturale di Genova
Genova Mus Zool. Anat. Comp Boll	Bollettino dei Musei di Zoologia e Anatomia Comparata della R. Universita di Genova
Genova, Soc. Ligust Atti	Atti della Societa Ligustica di Scienze Naturali e Geografiche
Genova Univ Atti	Atti della R Universita di Genova
Geogr. Soc. J.	Journal of the Royal Geographical Society of London
Geogr. Soc Proc.	Proceedings of the Royal Geographical Society and Monthly Record of Geography
Geogr Soc. Suppl. Pap	Royal Geograhical Society. Supplementary Papers
Geol. Mag.	Geological Magazine
Geol. Survey, Can	Geological Survey, Canada
Gera, Naturwiss Jahr	Jahresbericht der Gesellschaft von Freunden der Naturwissenschaften in Gera, nebst Nachrichten uber den Naturwissenschaftlichen Verein in Schleiz
Gerber	Der Gerber
Germar, Mag Entom	Magazin der Entomologie
Germar, Zts. Entom.	Zeitschrift fur die Entomologie
Gergonne, Ann Math.	Annales de Mathematique
Gesundh. Ing.	Gesundheits-Ingenieur
Gew. Ztg	Wieck's Gewerbezeitung
Gewerbebl Schw.	Schweizerisches Gewerbeblatt
Gewerbebl Wurt	Gewerbeblatt aus Wurttemberg
Gewerbeh	Gewerbehalle
Gewerks Ztg	Oesterreichische Gewerkszeitung
Giessen, Oberhess. Ges. Ber.	Berichte der Oberhessischen Gesellchaft für Natur- und Heilkunde
Gievel, Zts.	See Zts Gesammt. Naturwiss.
Gilbert, Ann Phys	See Ann. Phys.
Gill. Tech. Micro. Repos	Technical and Microscopical Repository
Giorn Arcad.	Giornale Arcadico di Scienze
Giorn farm. chim.	Giornale de farmacia, di chimica
Giorn Gen. civ	Giornale del Genio civile
Giron Ist. Lomb	See Bibl. Ital.
Giorn Mineral Crist Petr.	Giornale di Mineralogia, Cristallografia e Petrografia
Gironde Comm. Meteorol.	See Bordeaux Soc. Sci. Mem.
Gironde, J. Med.	Journal Medical de la Gironde
Gistl, Faunus	Faunus
Glasgow, Inst. Engin Trans.	Transactions of the Institution of Engineers and Shipbuilders in Scotland
Glasgow Med. Chir Soc Trans.	Transactions of the Medico-Chirurgical Society of Glasgow
Glasgow Med. J	Glasgow Medical Journal
Glasgow Natur. Hist Soc. Proc. & Trans.	Proceedings and Transactions of the Natural History Society of Glasgow
Glasgow Path Clin. Soc. Trans.	Transactions of the Glasgow Pathological and Clinical Society

Glasgow Phil. Soc. Proc.	Proceedings of the Philosophical Society of Glasgow
Glashütte	Glashutte, Die
Glas-Ind.	Glas-Industrie, Die
Gleanings Sci	Gleanings in Science
Globe	See Geneve Soc Geogr Mem.
Glückauf	Gluckauf; Berg- und Huttenmannische-Zeitschrift
Good Roads	Good Roads
Goodsir, Ann. Anat. Physiol.	Annals of Anatomy and Physiology
Gordon Coll. Phot. Assoc.	See Wombat.
Görlitz, Abh.	Abhandlungen der Naturforschenden Gesellschaft zu Gorlitz
Götheborg, Handl.	Gotheborgs Kongl. Vetenskaps och Vitterhets Samhalles Handlingar
Götheborg, Nya Handl.	Nya Handlingar af Kongl. Vettenskaps och Vitterhets Samhallet i Gotheborg
Göttingen, Abh.	Abhandlungen der Koniglichen Gesellschaft der Wissenschaften zu Gottingen
Göttingen, Comment.	Commentationes recentiores Societatis, etc
Göttingen, Nachr.	Nachrichten von der Georg-Augusts Universitat und der Konigl Gesellschaft der Wissenchaften zu Gottingen
Göttinger Studien	Gottinger Studien
Göttingen, Studien Ver.	Studien des Gottingischen Vereins Bergmannischer Freunde
Grafe, J. Chir. Augenheilk.	Journal der Chirurgie und Augen-Heilkunde
Graph. Mitth.	Schweizer graphische Mitteilungen
Graubunden Naturf. Ges. Jahr.	Jahresbericht der Naturforschenden Gesellschaft Graubundens
Gravenhage, Athenaeum	Athenaeum
Gravenhage, Inst. Ingen Tijdschr.	Tijdschrift van het Koninklijk Instituut van Ingenieurs
Gravenhage, Inst. Ingen. Uittrek.	Uittreksels uit Vreemde Tijdschriften voor de Leden van het Koninklijk Instituut van Ingenieurs
Gravenhage, Inst. Ingěn. Verh.	Verhandelingen van het Koninklijk Instituut van Ingenieurs
Gravenhage, Inst. Ingen Verslag.	K. Instituut van Ingenieurs. Algemeen Verslag van de Werkzaamheden en Notulen der Vergaderingen
Gravenhage, Tijdschr.	Tijdschrift voor Entomologie, door de Nederlandsche Entomologische Vereeniging
Graves, Natur. J.	The Naturalists' Journal and Miscellany
Graz Bot. Inst. Mitth.	Mittheilungen aus dem Botanischen Institute zu Graz
Graz, Unters. Physiol Histol.	Untersuchungen aus dem Institute fur Physiologie und Histologie
Great. Brit. Phil. Soc.	See Victoria Inst. J.
Greifswald Naturwiss. Ver. Mitth.	See Neu-Vorpommern Mitth.
Grenoble, Acad. Delph. Bull.	Bulletin de l'Academie Delphinale, ou Société des Sciences et Arts de Grenoble
Grevillea	Grevillea, a Quarterly Record of Cryptogamic Botany and its Literature
Groningen, Ann. Acad.	Annales Academiae Groninganae
Gruithuisen, Neue Analekt.	Neue Analekten fur Erd- und Himmels-kunde
Grunert Archiv.	Archiv für Mathematik und Physik
Grunert, Meteor. Optik	Beiträge zur meteorologischen Optik, etc.
Guat. P.	Guatemala Patent

Guia Minero	Guia del Minero. Periodico cientifico, industrial y mercantil
Guillemin, Archiv. Bot.	Archives de Botanique, ou Recueil Mensuel de Memoires originaux, etc.
Gummi-Ztg	Gummi-Zeitung
Gunsburg, Zts. Klin Med	Zeitschrift für klinische Medizin, mit dem Verein für physiologische Heilkunde in Breslau
Gurlt, Mag. Ges. Thierheilk	Magazin fur die gesammte Thier-Heilkunde
Guy's Hosp Rep.	Guy's Hospital Reports
Haarlem Kolon. Mus Bull	Bulletin van het Koloniaal Museum te Haarlem
Haarlem, Mus. Teyler Archiv.	Archives du Musee Teyler
Haarlem, Natuurk. Verh. Maatsch. Wet.	Natuurkundige Verhandelingen van de (Bataafsch) Hollandsche Maatschappij der Wetenschappente Haarlem
Haaxman, Tijdschr.	Tijdschrift voor Wettenschappelijke Pharmacie, etc.
Habana Acad Anales.	Anales de la (Real) Academie de Ciencias Medicaes Fisicas y Naturales de la Habana
Haeser, Archiv. Med.	Archiv fur die gesammte Medicin
Hage	See Gravenhage
Hahnemann Month.	Hahnemannian Monthly, Philadelphia
Haidinger, Abh.	Naturwissenschaftliche Abhandlungen
Haidinger, Ber.	Berichte uber die Mittheilungen von Freunden der Naturwissenschaften in Wien
Hainaut Soc Mem.	Memoires et Publications de la Société des Sciences, des Arts et des Lettres du Hainaut
Hall, Bijdragen	Bijdragen tot de Natuurkundige Wetenschappen
Halle, Abr. Naturwiss. Ver.	Abhandlungen des Naturwissenschaftlichen Vereins fur Sachsen und Thuringen in Halle
Halle aux cuirs, La	Halle aux cuirs, La
Halle, Jahr. Naturwiss. Ver.	Jahresbericht des Naturwissenshaftlichen Vereins in Halle
Halle Kryptog. Lab.	See Beitr. Physiol Morphol.
Halle, Naturf. Ges. Abh.	Abhandlungen der Naturforschenden Gesellschaft zu Halle
Halle, Naturf. Ges. Ber.	Bericht der Naturforschenden Gesellschaft zu Halle
Halle, Naturf. Ges. Neu. Schr.	Neue Schriften der Naturforschenden Gesellschaft zu Halle
Halle, Zts. Ges. Naturwiss.	Zeitschrift fur die gesammten Naturwissenschaften
Hamburg, Abh. Geb. Naturwiss.	Abhandlungen aus dem Gebiete der Naturwissenschaften
Hamburg Bot. Ges.	See Bot. Centrbl.
Hamburg, Mitth.	Mittheilungen aus den Verhandlungen der Naturwissenschaftlichen Gesellschaft in Hamburg
Hamb. Mus. Ber.	Naturhistorisches Museum zu Hamburg. Berichte
Hamb. Mus. Jahr.	Jahresbericht uber das Naturhistorische Museum zu Hamburg
Hamb. Mus Mitth.	Mittheilung aus dem Naturhistorischen Museum in Hamburg
Hamb. Naturwiss. Ver. Abh.	Abhandlungen aus dem Gebiete der Naturwissenschaften herausgegeben vom Naturwissenschaftlichen Verein in Hamburg
Hamb. Ver. Naturwiss. Unterh. Verh.	Verhandlungen des Vereins für Naturwissenschaftliche Unterhaltung zu Hamburg
Hamb. Wiss. Anst. Jahr.	Jahrbuch der Hamburgischen Wissenschaftlichen Anstalten

Hampshire Field Club Pap. & Proc.	Papers and Proceedings of the Hampshire Field Club
Hannover Architekt -Ver. Zts.	Zeitschrift des Architekten- und Ingenieur-Vereins zu Hannover. Zeitschrift fur Architektur und Ingenieurwesen
Hannover Jahr.	...Jahresbericht der Naturhistorischen Gesellschaft zu Hannover
Hannöverische Ann.	Hannoverische Annalen fur die gesammte Heilkunde
Harlem Soc. Holland. Sci.	See Arch. Neerland
Hartford, Trans.	Transactions of the Natural History Society of Hartford
Harvard Mus. Zool. Mem.	Memoirs of the Museum of Comparative Zoology at Harvard College
Harvard Mus. Zool Bull.	Bulletin of the Museum of Comparative Zoology at Harvard College, in Cambridge
Harz, Naturwiss. Ver. Ber.	Berichte des Naturwissenschaftlichen Vereins des Harzes zu Blankenburg
Havre, Cercle Bot.	Cercle pratique d'Horticulture et de Botanique de l'arrondissement du Havre. Bulletins
Haw. P.	Hawaiian Patent
Haye	See Congr. Int. Hyg. C. R, 1884
Heart	Heart
Hedwigia	Hedwigia. Ein Notizblatt fur Kryptogamische Studien nebst Repertorium fur Kryptogamische Literatur. Hedwigia. Organ fur (specielle) Kryptogamenkunde (und Phytopathologie) nebst Repertorium fur (Kryptogamische) Literatur.
Heidelb. Jahr. Lit.	Jahrbucher der Literatur. Verhandlungen des Naturhistorisch-Medicinischen Vereins zu Heidelberg
Heidelb. Naturhist. Med. Festschr.	Festchrift zur Feier des funfhundertjahrigen Bestehens der Ruperto-Carola dargebracht von dem Naturhistorisch-Medicinischen Verein zu Heidelberg
Heidelb. Naturhist. Med Verh.	Verhandlungen des Naturhistorisch-Medicinischen Vereins au Heidelberg
Heidelb, Verh.	Verhandlungen der in Heidelberg versammelten Augenarzte
Heis, Wochenschr.	Wochenschrift für Astronomie, Meteorologie, und Geographie
Heller, Archiv.	Archiv fur physiologische und pathologische Chemie und Mikroskopie
Helsingfors, Acta Soc. Sci. Fenn.	Acta Societatis Scientiarum Fennicae
Helsingfors, Bidrag Finlands Natur o Folk.	Bidrag till kannedom om Finlands Natur och Folk, utgifna af Finska Vetenskaps-Societeten
Helsingfors, Bidrag Finlands Naturkänn.	Bidrag till Finlands Naturkannedom, Etnografi och Statistik, utgifna af Finska Vetenskaps-Societeten
Helsingfors, Faun. Flor. Fenn. Acta.	Acta Societatis pro Fauna et Flora Fennica
Helsingfors, Fauna Flora Fenn. Medd.	Meddelanden af Societas pro Fauna et Flora Fennica
Helsingfors, Faun. Flor. Fenn. Notiser	Notiser ur Sallskapets pro Fauna et Flora Feennica Forhandlingar
Helsingfors, Öfvers, Finaka Vet. Soc.	Öfversigt af Finska Vetenskaps-Societatens Förhandlingar
Helv. Chim. Acta	Helvetica Chimica Acta
Henle und Pfeufer, Zts.	See Zeitschrift fur rationelle Medicin
Hermannstader Verh.	Verhandlungen und Mittheilungen des Siebenbürgischen Vereins für Naturwissenschaften in Hermannstadt

Hermbstätt, Archiv.	Archiv der Agriculturchemie für denkende Landwirthe
Hermstädt, Bull.	Bulletin des Neuesten und Wissenwürdigsten aus der Naturwissenschaft, etc.
Hermbstadt, Museum	Museum des Neuesten und Wissenwurdigsten aus dem Gebiete der Naturwissenschaft, der Künste, der Fabriken, der Manufakturen, der technischen Gewerbe, der Landwirthschaft, der Produktenwaaren und Handelskunde, und der bürgerlichen Haushaltung, &c
Hertha	Hertha
Herts. Natur. Hist. Soc. Trans.	Transactions of the Hertfordshire Natural History Society and Field Club
Hessen, Naturhist. Verg.	Verhandlungen des Naturhistorischen Vereins für das Gross herzogthum Hessen und Umgebung
Heusinger, Zts.	Zeitschrift für die organische Physik
Hide and Leather	Hide and Leather
High Wycombe Natur. Hist. Mag.	The Quarterly Magazine of the High Wycombe Natural History Society
Highland Soc. Trans.	Transactions of the Highland and Agricultural Society of Scotland with an abstract of the Proceedings
Hildesheim Roemer-Mus. Mitth.	Mittheilungen aus dem Roemer-Museum Hildesheim
Himly, Bibl. Ophthalm.	Bibliothek fur Ophthalmologie
Hippone	See Bone
Hisinger, Afh.	Afhandlingar i Fysik, Kemi, och Mineralogie
Hobart Town	See Tasmania
Hoeven en Vriese, Tijdschr.	Tijdschrift voor Natuurlijke Geschiedenis en Physiologie
Hoff, Mag.	Magazin fur die gesammte Mineralogie, Geognosie, etc.
Hoffman, Phytogr Blatt.	Phytographische Blatter
Holl. P.	Holland Patent
Holländ, Beitr.	Hollandsiche Beiträge zu den anatomischen und physiologischen Wissenscaften
Holland, Mag.	Hollandisches Magazin der Naturkunde
Holmesdale Natur. Hist. Club Proc.	Proceedings and Annual Reports of the Holmesdale Natural History Club, Reigate, for the years 1865–67
Homme	L'Homme: Journal illustre des Sciences Anthropologiques
Hooker, Bot. Miscell.	The Botanical Miscellany
Hooker, Comp. Bot. Mag.	Companion to the Botanical Magazine
Hooker, Lond. J. Bot.	London Journal of Botany
Hoppe, Bot. Taschenb.	Neues Botanisches Taschenbuch für die Anfanger dieser Wissenschaft und der Apothekerkunst
Horae Soc. Entom. Rossicae	Horae Societatis Entomologicae Rossicae variis sermonibus Rossicae usitatis
Horkel, Archiv.	Archiv. für die thierische Chemie
Horn, Archiv. Med.	Archiv. fur praktische Medizin und Klinik
Horn's Phot. J.	Horn's photographisches Journal
Hornschuch, Archiv.	Archiv Skandinavischer Beitrage zur Naturgeschichte
Horolog. J.	The Horological Journal
Hortic. Soc. J.	Journal of the Royal Horticultural Society of London
Hortic. Soc. Trans.	Transactions of the Horticultural Society of London
Hufeland, J. Arzn.	Journal der practischen Arzneikunde
Humboldt.	Humboldt. Monatsschrift fur die Gesamten Naturwissenschaften
Humming Bird	The Humming Bird. .... scientific, artistic and industrial Review

Hongkong P.	Hongkong Patent
Hung. P.	Hungarian Patent
Hutm. Ztg	Deutsche Hutmacher-Zeitung
Hyg. Congr.	See Congr. Int. Hig. Act.; Congr. Int. Hyg. C. R.; Int. Congr. Hyg. Arb.; Int. Congr. Hyg. Trans.
Hyg. Rundschau.	Hygienische Rundschau. Berlin
Hyg. viande	Hygiene de la viande et du lait, L'
Iekaterinenb., Soc. Oural. Bull.	Bulletin de la Société Ouralienne d'Amateurs des Sciences Naturelles
Il Berico	Il Berico
Il Cimento	Il Cimento
Il. Giamb-Vico	Il Giambattista-Vico
Il Progresso	Il Progresso delle Scienze, Lettere, ed Arti.
Il Subalpino	Il Subalpino, Giornale di Scienze
Il Tempo	Il Tempo, Giornale Italiano di Medicina
Ill. Insects Rep.	...Report of the State Entomologist . on the Noxious and Beneficial Insects of the State of Illinois
Ill Lab. Natur. Hist. Bull.	Bulletin of the Illinois State Laboratory of Natural History
Ill. Mus Natur. Hist Bull.	Bulletin . of the Illinois State Museum of Natural History
Illiger, Magazin	Magazin für Insektenkunde
Illumin Engin. (London)	Illuminating Engineer (London), The
Illust. Hortic	Illustration horticole, journal special des Serres et des Jardins
Illust landw. Ztg.	Illustrierte landwirtschaftliche Zeitung
Illust. Off. J.	Illustrated Official Journal, The (Patents)
Illust. Wochenschr. Entom	Illustrierte Wochenschrift für Entomologie Internationales Organ fur alle Interessen der Insektenkunde. Offizielles Organ der Berliner Entomologischen Gesellschaft
Impr	L'imprimerie
Ind. Chim.	Industria chimica
Ind. lait.	L'Industrie laitiere
Ind. Text.	L'industrie textile
Ind. Ztg.	Deutsche Industrie Zeitung
Index Med.	Index Medicus, Washington
India Agric. Soc J.	Journal of the Agricultural and Horticultural Society of India
India, Agric. Soc Proc.	Proceedings of the Agricultural and Horticultural Society of India
India Agric. Soc. Trans.	Transactions of the Agricultural and Horticultural Society of India
India Bot. Surv. Records	Records of the Botanical Survey of India
India Dept. Agric.	India Department of Agriculture, Publications
India, Govt. Records (For. Dept.)	Selections from the Records of the Government of India. (Foreign Department)
India, Govt. Records (Home Dept)	Selections from the Records of the Government of India
India P.	Indian Patent
India Rev.	India Review and Journal of Foreign Science and the Arts
India Rub. J.	India Rubber Journal
India Rub. World	India Rubber World
Indian Ann.	Indian Annals of Medical Science
Indian J. Med. Phys. Sci.	Indian Journal of Medical Science
Indian Med. Gaz.	The Indian Medical Gazette, a monthly record of Medicine, &c.

Indian Meteorol. Mem.	Indian Meteorological Memoirs: being occasional Discussions and Compilations of meteorological data relating to India and the neighboring countries
Indian Mus. Notes	Indian Museum Notes
Industrieztg. Ungarn	Industriezeitung fur Ungarn
Ingenieur	Der Ingenieur
Inghirami, Opuscoli	Nuova Collezione di Opuscoli e Notizie di Scienze
Innsbruck, Jahr.	Jahresbericht der k. k. Ober-Realschule zu Innsbruck
Innsbruck Naturwiss. Med. Ber.	Berichte des Naturwissenschaftlich-medizinischen Vereines in Innsbruck
Innsbruck, Neue Zts.	Neue Zeitschrift des Ferdinandeums für Tirol
Innsbruck, Zts. Ferdinandeums	Zeitschrift des Ferdinandeums fur Tirol und Voralberg
Inst.	L'Institut
Inst. Act. J.	Journal of the Institute of Actuaries (and Assurance Magazine)
Inst. Brewing Trans.	Transactions of the Institute of Brewing
Inst. Civ. Eng. Proc.	Minutes of the Proceedings of the Institution of Civil Engineers
Inst. Egypt. Bull.	Bulletin de l'Institut Egyptien
Inst. Egypt. Mem.	Memoires (ou Travaux originaux) presentes (et lus) a l'Institut Egyptien
Inst. Elect. Engin. J.	Journal of the Institution of Electrical Engineers
Inst. Mechan. Engin. Proc.	Institution of Mechanical Engineers. Proceedings
Inst. Min Eng Trans	Transactions of the Institution of Mining Engineers
Inst. Min. Met. Trans.	Transactions of the Institution of Mining and Metallurgy
Inst. Solvay Trav.	Institut Solvay. Travaux de Laboratoire
Intell. Observer	The Intellectual Observer
Intl Beitr. Path. Therap.	Internationale Beitrage zur Pathologie und Therapie, die Ernährungsstörungen, Stoffwechsel und Verdauungkrankheiten
Intl. Congr Appl Chem.	International Congress of Applied Chemistry
Intl. Congr Hyg. Trans.	Transactions of the International Congress of Hygiene and Demography
Intl. Congr Zool Proc.	Proceedings International Congress of Zoology
Intl. Entom. Ver.	See Zürich, Soc. Ent.
Intl. Med. Congr. Trans	Transactions of the International Medical Congress
Intl. Med. Congr Verh.	Verhandlungen des Internationalen Medicinischen Congresses
Intl. J. Anat.	Monthly International Journal of Anatomy and Histology (Physiology)
Intl. Mschr. Anat.	See Intl. J. Anat.
Intl. Sugar J.	International Sugar Journal, The
Intl. Zentr. Baukeram. Glasind	Internationales Zentralblatt für Baukeramik und Glasindustrie
Intl. Zts. Metallog.	Internationale Zeitschrift für Metallographie
Invent. Rec.	Inventor's Record, The
Iowa Acad. Sci. Proc.	Proceedings of the Iowa Academy of Sciences
Iowa Univ. Lab. Natur. Hist. Bull.	Bulletin from the Laboratories of Natural History of the State University of Iowa
Ireland, Coll. Physicians Trans.	Transactions of the Association of Fellows and Licentiates of the King's and Queen's College of Physicians in Ireland
Ireland, Inst. Civ. Eng. Trans.	The Transactions of the Institute of Civil Engineers of Ireland

Ireland Roy. Soc. Ant. Proc. & Pap.	See Dublin, Roy. Soc. Ant. Ir. Jl.
Ireland Zool. Soc.	See Irish Natlist
Iris	Correspondenz-Blatt des Entomologischen Vereins Iris zu Dresden Iris, Dresden. Deutsche Entomologische Zeitschrift herausgegeben von der Gesellschaft Iris zu Dresden in Verbindung mit der Deutschen Entomologischen Gesellschaft zu Berlin. . Fortsetzung des "Correspondenz-Blattes des Entomologischen Vereins Iris"
Irish Acad. Cunningham Mem.	Royal Irish Academy. Cunningham Memoirs
Irish Acad. Proc.	Proceedings of the Royal Irish Academy
Irish Acad. Trans.	The Transactions of the Royal Irish Academy
Irish Natur.	The Irish Naturalist: a monthly Journal of general Irish Natural History
Iron	Iron
Iron Age	Iron Age
Iron Coal Trades Rev.	Iron Coal Trades Review
Iron Steel Inst. J.	The Journal of the Iron & Steel Institute
Iron Steel Inst Trans.	Transactions of the Iron and Steel Institute
Isenflamm, Beitr. Zerglied.	Beitrage fur die Zergliederungskunst
Isere Soc. Bull.	Bulletin de la Société de Statistique, des Sciences naturelles et des Arts industriels du Departement de l'Isere
Isle of Man Natur Hist. & Antiq. Soc.	See Yn Lioar Manninagh
Ital. P.	Italian Patent
Italia, Soc. Bot. Bull.	Bullettino della Societa Botanica Italiana
Italia Soc. Crittog. Atti	Atti della Societa Crittogamologica Italiana
Italia Soc. Crittog Comment.	Commentario della Societa Crittogamologica Italiana
Italia Soc. Crittog Mem.	Memorie della Societa Crittogamologica Italiana
Italia, Soc. Entom Bull.	Bullettino della Societa Entomologica Italiana
Italia, Soc Zool Boll	Bollettino della Societa Zoologica Italiana
Ithaca, Cornell Univ Bull. Amer. Paleont.	Bulletins of American Paleontology
J.	Journal
J. A. C. S.	Journal of the American Chemical Society
J. Adv. Therap.	Journal of Advanced Therapeutics, New York
J Agric.	The (Quarterly) Journal of Agriculture
J. agric. Hort.	Journal de l'Agriculture, le Horticulture, etc.
J. Agric. Prat.	Journal d'Agriculture pratique, etc.
J. Agric Sci.	Journal of Agricultural Science
J. agric. Soc.	Journal of the Agricultural Society
J. Agric. Tropicale	Journal d'Agriculture tropicale
J. allied Soc.	Journal of the Allied Societies (Dental)
J. Amer. Lea. Chem. Assoc.	Journal of the American Leather Chemists' Association
J. Amer. Med. Assoc.	Journal of the American Medical Association
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association
J. Amer. Soc. Mechan. Eng.	Journal of the American Society of Mechanical Engineers
J. Anal. Chem.	The Journal of Analytical (and Applied) Chemistry
J. Anat.	Journal de l'anatomie de la Physiologie normales et pathologiques de l'homme et des animaux
J. Anat. Physiol.	The Journal of Anatomy and Physiology
J. Appl. Chem.	Journal of Applied Chemistry

J. Appl. Micr	*Journal of Applied Microscopy*
J. Assoc. Eng. Soc.	*Journal of the Association of Engineering Societies*
J. Biol. Chem.	Journal of Biological Chemistry
J. Bot.	Journal de Botanique
J. Buchdr.	Journal fur Buchdruckerkunst
J. C. S.	Journal of the Chemical Society, London
J. Camera Club	Journal of the Camera Club
J. Can Min Inst.	Journal of the Canadian Mining Institutes
J. Chem Met. Soc. South Af.	Journal of the Chemical, Metallurgical and Mining Society of South Africa
J. chim. med.	Journal de chimie medicale, de pharmacie et de toxicologie
J. chim. phys.	Journal de chimie, physique, electrochemie, thermochimie, radiochimie, mechanique, chimie, stoichiometrie
J. Chir.	Journal de Chirurgie
J. Chir. Augenheilk.	Journal der Chirurgie und Augenheilkunde
J Coll. Agric. Imp Univ. Tokyo	Journal of the College of Agriculture, Imperial University of Tokyo
J Comp. Path Therap	The Journal of Comparative Pathology and Therapeutics
J Conch	The Journal of Conchology
J. ecole poly.	Journal de l'Ecole polytechnique
J. Entom.	Journal of Entomology, descriptive and geographical
J. Exp. Med.	Journal of Experimental Medicine
J. Exp. Zool.	Journal of Experimental Zoology, The
J. fabr. sucre	Journal des fabricants de sucre
J. Frank. Inst	Journal of the Franklin Institute
J Gasbeleucht	Journal fur Gasbeleuchtung
J. Gaslighting	Journal of Gas Lighting
J. Gen. Physiol	Journal of General Physiology
J Genie Civ.	Journal du Genie Civil des Sciences et des Arts
J. Geol	Journal of Geology
J. Goldschm.	Journal der Goldschmiedekunst und verwandter Gewerbe
J. Heb Med	Journal Hebdomadaire de Medecine
J. Heb. Sci. Med.	Journal Hebdomadaire des Progres des Sciences et Institutions Medicales
J. Home Econ.	Journal of Home Economics, The
J. Hygiene	Journal of Hygiene
J. Ind Eng. Chem.	Journal of Industrial and Engineering Chemistry
J. Indian Archipel.	Journal of the Indian Archipelago and Eastern Asia
J. Infect. Dis.	Journal of Infectious Diseases
J Inst. Brewing	Journal of the Institute of Brewing
J. Inst. Metals	Journal of the Institute of Metals
J Intl. Anat.	See Int. J. Anat.
J. Invent.	Journal des Inventeurs
J. Landw.	Journal für Landwirtschaft
J. Med. Chir. Pharm.	Journal de Medecine, Chirurgie, Pharmacie
J. Med Paris	Journal de medicine de Paris
J. Med. Research	Journal of Medical Research
J. Microgr	Journal de micrographie
J. Micro. Sci.	Quarterly Journal of Microscopical Science
J. Mines	Journal des Mines, ou Recueil de Memoires sur l'exploitation des Mines, et sur les Sciences et les Arts qui s'y rapportent
J. mines met.	Journal des mines et de metallurgie
J. Morphol.	Journal of Morphology

J. Mus. Godeffroy	Journal des Museum Godeffroy. Geographische, Ethnographische und Naturwissenschaftliche Mittheilungen
J. Mycol.	The Journal of Mycology
J. N. Engl. Water Works Assoc.	Journal New England Water Works Association
J. Opthalmol.	Journal d'Ophthalmologie
J. Ornith.	Journal fur Ornithologie
J. Papier	Journal de Fabricants de Papier, fonde et publie par L. Piette
J. Path. Bact.	The Journal of Pathology and Bacteriology
J. Petrole	Journal du petrole
J. Pharm.	Journal de Pharmacie
J. Pharm. Anvers	Journal de Pharmacie d'Anvers
J. Pharm. Chim.	Journal de Pharmacie et de Chimie
J. Pharm. Elsass-Lothringen	Journal de pharmacie von Elsass-Lothringen
J. Pharm. Soc Japan	Yakagakuzasshi (Journal of the pharmaceutical society of Japan)
J. Pharmacol.	Journal of Pharmcology and Experimental Therapeutics
J. Phot. Suppl.	Journal of Photographic Supplies
J. Phot. Soc.	Journal of the Photographic Society
J. Phys.	Journal de Physique theorique et appliquee
J. Phys. Chem.	The Journal of Physical Chemistry
J. Phys. Chim.	Journal de Physique, de Chimie, et de l'Histoire Naturelle
J. Physiol.	The Journal of Physiology
J. physiol path gen.	Journal de physiologie et de pathologie general, Paris
J. prakt. Chem	Erdmann's Journal fur praktische Chemie
J. Psychol Med	Journal of Psychological Medicine and Mental Pathology
J. Roy Agric Soc	Journal of the Royal Agricultural Society
J. Roy. Astron Soc. Canada	Journal of the Royal Astronomical Society of Canada
J. Roy. Inst Pub. Health	Journal of the Royal Institute of Public Health
J. Roy. San. Inst.	Journal of the Royal Sanitary Institute
J. Roy. Soc. N. S. Wales	Journal of the Royal Society of New South Whales
J. Roy. U. S. Inst	Journal Royal United Service Institution
J. Russ. Phys. Chem Soc.	Journal of the Russian Physical Chemical Society
J. S. C. I.	Journal of the Society of Chemical Industry
J. Savants	Journal des Savants
J. Sci.	The Journal of Science
J. sci math. physi. nat.	Journal de sciencias mathematicas, physicas naturaes
J. Soc. Arts	Journal of the Royal Society of Arts
J. Soc. Dyers Col.	Journal of the Society of Dyers and Colorists
J. soc. pharm. Anvers	Journal de pharmacie, organe de la société de pharmacie d'Anvers
J. Soc. Telegr. Eng.	Journal of the Society of Telegraphic Engineers
J. State Med.	The Journal of State Medicine
J. suisse chim. pharm.	Journal suisse de chimie et pharmacie
J. Travel	The Journal of Travel and Natural History
J. Trop. Med.	The Journal of Tropical Medicine
J. U. S. Artill.	Journal of the United States Artillery
J. Univ. Med.	Journal universel et hebdomadaire de Medecine et de Chirurgie pratiques et des Institutions medicales
J. Univ. Sci. Med.	Journal Universel des Sciences Medicales
J. Wash. Acad. Sci.	Journal of the Washington Academy of Sciences
J. Western Soc. Eng.	Journal of the Western Society of Engineers

Jaarb. Mijnw. Nederl. Ind.	Jaarboek van het Mijnwezen in Nerderlandsch Oost-Indie
Jahr. = Jahresbericht	Jahrbuch
Jahr Agrik.-Chem	Jahresbericht uber die Fortschritte der Agrikulturchemie mit besonderer Berucksichtigung der Pflanzenchemie und Pflanzenphysiologie
Jahr. Berg- u. Huttenw.	Jahrbuch fur das Berg- und Huttenwesen im Königreiche Sachsen
Jahr. Kinderheilk.	Jahrbuch für Kinderheilkunde und physische Erziehung
Jahr. Chem.	Jahresbericht der Chemie (Liebig-Kopp)
Jahr. Gahr. Organ.	Jahresbericht uber die Fortschritte in der Lehre von den Gahrungs-Organismen (Koch)
Jahr. Mineral	Neues Jahrbuch fur Mineralogie, Geologie und Palaeontologie
Jahr. Mineral Beil.-Bd	Neues Jahrbuch fur Mineralogie, Geologie, und Palaeontologie, Beilage-Band
Jahr Pharm.	Jahresbericht der Pharmacie
Jahr. Phot.	Jahrbuch der Photographie (Eder)
Jahr. Phot. Reprod.	Jahrbuch fur Photographie und Reproduktiontechnik
Jahr. Phy. Ver. Frankfurt	See Frankfurt, Jahr. Phys. Ver.
Jahr. Physiol.	Jahresbericht uber die Fortschritte der Physiologie
Jahr. Radioactiv. Electronik.	Jahrbuch der Radioaktivität und Electronik
Jahr. rein. Chem.	Jahresbericht der reinen Chemie
Jahr. Tier-Chem.	Jahresbericht uber der Fortschritte der Tier-Chemie
Jahr. wiss. Bot.	Jahrbucher fur wissenschaftliche Botanik
Jamaica Inst. J.	Journal of the Institute of Jamaica
Jamaica P.	Jamaica Patent
Jamaica Soc. Arts. Trans.	Transactions of the Jamaica Society of Arts
Jamain, Archives Ophthalm.	Archives d'Ophthalmolgie
Jap P.	Japanese Patent
Jardine, Mag Zool. Bot.	The Magazine of Zoology and Botany
Jena Ann. Acad.	Annales Academiae Jenensis
Jena Ann. Phys. Med.	Die Jenaischen Annalen fur Physiologie und Medicin
Jena Ann. Soc. Mineral	Annalen der Societät fur die gesammte Mineralogie zu Jena
Jena Denkschr.	Denkschriften der Medicinisch-Naturwissenschaftlichen Gesellschaft zu Jena
Jena Geogr. Ges. Mitth.	Mittheilungen der geographischen Gesellschaft (fur Thuringen) zu Jena
Jena Sitzber.	Sitzungsberichte der Jenaischen. Gesellschaft für Medicin und Naturwissenschaft
Jena Zts.	Jenaische Zeitschrift fur Naturwissenschaft herausgegeben von der Medicinisch-naturwissenschaftlichen Gesellschaft zu Jena
Jern-Kontoret's Ann.	Jern-Kontoret's Annaler
Johns Hopkins Biol. Lab. Mem.	Memoirs from the biological laboratory of the Johns Hopkins University
Johns Hopkins Biol. Lab. Stud.	Johns Hopkins University. Studies from the Biological Laboratory
Johns Hopkins Univ. Circ.	The Johns Hopkins University Circulars
Jura, Trav. Soc. Emul.	Travaux de la Société d'Émulation du Department du Jura
Jurjew	See Dorpat
Just's bot. Jahr.	Just's botanischer Jahresbericht, Leipzig and Berlin
Kali	Kali

Kampen, Mag.	Magazin voor Wetenschappen, Kunsten, &c.
Kan. Acad. Sci. Trans.	Transactions of the....annual meeting of the Kansas Academy of Science
Kan. Univ. Quart.	The Kansas University Quarterly
Karlsruhe Bact. Inst. Arb.	Arbeiten aus dem bacteriologischen Institut der technischen Hochschule zu Karlsruhe
Karlsruhe Naturwiss. Ver. Verh.	Verhandlungen des Naturwissenschaftlischen Vereins in Karlsruhe
Kàrnten, Berg-Verein, Zts.	Zeitschrift des Berg- u. Huttenmannischen Vereins fur Karnten
Karnten Landesmus. Jahr.	Jahrbuch des naturhistorischen Landes-Museums von Karnten
Kàrnten, Zts.	Zeitschrift des berg- und huttenmannischen Vereines fur Karnten
Karsten	See Botan. Untersuch.
Karsten, Archiv.	Archiv fur Mineralogie, Geognosie, Bergbau, und Huttenkunde
Kassel Ver. Naturk. Ber.	Bericht des Vereins fur Naturkunde zu Cassel
Kassel Ver. Naturk. Festschr.	Festschrift des Vereins fur Naturkunde zu Cassel zur Feier seines Funfzigjahrigen Bestehens
Kastner, Archiv. Chem.	Archiv. fur Chemie und Meteorologie
Kastner, Archiv. Naturlehre	Archiv. fur die gesammte Naturlehre
Kazan Soc. Phys.-Math. Bull.	Bulletin de la Société Physico-Mathematique de Kazan
Kazan Soc. Natur Proc.	Proceedings of the Physico-Mathematical Section of the Society of Naturalists of the Imperial University of Kazan
Kazan Soc. Natur. Trans.	Transactions of the Society of Naturalists of the Imperial University of Kazan
Kazan Univ. Bull.	Bulletin of the Imperial University of Kazan
Kazan Univ. Mem.	Scientific Memoirs of the Imperial University of Kazan
Kekule, Krit Zts Chem.	Kritische Zeitschrift fur Chemie, Physik, und Mathematik; see also Zts. Chem.
Keram. Rundschau	Keramische Rundschau
Kew Bull.	Royal (Botanic) Gardens, Kew. Bulletin of Miscellaneous Information
Kharkov. Math. Soc. Commun.	Communications de la Société Mathematique de Kharkov
Kiel Mitth. Ver. Elbe.	Mittheilungen des Vereins nordlich der Elbe zur Verbreitung naturwissenschaftlicher Kenntnisse in Kiel
Kiel, Physiol. Inst. Arb.	Arbeiten aus dem Kieler physiologischen Institut
Kiel, Schr.	Schriften der Universität zu Kiel
Kiel Univ. Mineral. Inst. Mitth.	Mittheilungen aus dem Mineralogischen Institut der Universitat Kiel
Kiev Soc. Natur. Mem.	Memoires de la Société des Naturalistes de Kiev
Kiobenh. Bot. For.	See Bot. Tidsskr.
Kiöbenh. Bot. For. Festskr.	Festskrift, udgivet af den Botaniske Forening i Kiobenhavn i Anledning af dens Halvhundredaars fest, den 12 April, 1890
Kiobenh. Bot. For. Medd.	Meddelelser fra den Botaniske Forening i Kjobenhavn
Kiöbenh. Carlsb. Lab. Medd.	Meddelelser fra Carlsberg Laboratoriet
Kiöbenh. Dansk. Vid. Selsk. Afh.	Det Kongelige Danske Videnskabernes Selskabs naturvidenskabelige og mathematiske Afhandlinger

Kiobenh., Dansk. Vid Selsk. Skrift.	Det Kongelige Danske Videnskabernes Selskabs Skrifter. Naturvidenskabelig og Mathematisk Afdeling
Kiöbenh. Ent. For.	See Ent. Medd. (Kiobenh.)
Kiöbenh., Oversigt	Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlinger og dets Medlemmers Arbejder i Aaret 1874(-83)...samt. med en Résumé du *Bulletin de l'Academie Royale Danoise des Sciences et des Lettres* pout l'annee 1874(-83)
Kiobenh., Reg. Soc. Med Acta.	Acta Regiae Societatis Medicae Havniensis
Kiobenh., Vidensk. Forh.	Videnskabelige Forhandlinger ved Sioelland Stifts Landemde
Kiobenh, Vidensk. Meddel	Videnskabelige Meddelelser fra den Naturhistoriske Forening i Kjobenhavn
K. K. Ges. Aerzte	See Med Jahr
Klausenburg	See Kolozsvar
Kliniek	Kliniek
Klug, Jahr. Insect.	Jahrbucher der Insectenkunde, etc
Koll Chem. Beihefte	Kolloidchemische Beihefte
Kolloid-Zts.	Kolloid-Zeitschrift
Kolozsvar Orvos-Termesz Tars Ertes	Ertesito a "Kolozsvari Orvos-Termeszettudomanyi Tarsulat" -nak az . . orvosi, termeszettudomanyi szakuleseirol . Proceedings of the Medical and natural history sections of the Klausenburg Medical and Natural History Society
K Svenska Vet-Akad.	Kongl Svenska Vetenskaps Akademiens Handlingar
Konigsb. Archiv.	Konigsberger Archiv fur Naturwissenschafften und Mathematik
Konigsb Med Jahr.	Konigsberger medicinische Jahrbucher; herausgegeben von dem Verein für wissenschaftliche Heilkunde zu Konigsberg
Konigsb Schr.	Schriften der physikalisch-okonomischen Gesellschaft zu Konigsberg in Preussen
Kosmos (Lwow)	Kosmos. Czasopismo polskiego Towarzystwa przyrodnikow imienia Kopernika. (Cosmos. The Journal of the Polish Society Naturalists founded in honor of Copernicus)
Krain Mus-Ver Mitth	See Laibach, Mus.-Ver. Krain Mitth.
Krakow Akad. (Mat Przyrod) Pam.	Pametnik Akademii Umiejetnosci w Krakowie. Wydzial Matematyczno-Przyrodniczy. (Memoires of the Academy of Science in Cracow. Section of Mathematics and Natural Science)
Krakow Akad (Mat -Przyrod) Rozpr	Rozprawy i Spawozdania z Posiedzen Wydzialu Matematyczno-Przyrodniczego Akademii Umiejetnosci (Proceedings of the Section of Mathematics and Natural Science of the Academy of Science)
Krakow, Akad. (Mat - Przyrod.) Rozpr. & Spraw.	Rozprawy i Sprawozdania z Posiedzen Wydzialu Matematyczno-Przyrodniczego Akademii Umiejetnosci (Proceedings of the Section of Mathematics and Natural Science of the Academy of Science)
Krakow Kom. Fizyogr. Spraw.	Akademija Umiejetnosci w Krakowie. Sprawozdanie Komisyi Fizyograficznej .... (Academy of Science in Cracow. Report of the Physiographical Commission)
Krakow, Roczn. Tow. Nauk.	Rocznik Towarzystwa Naukowego z Uniwersytetem Jagiellonskim Zlaczonego
Krakau, Untersuch Path.	Untersuchungen aus dem Pathologisch-Anatomischen Institute in Krakau

Kreutzer's Jahr. Phot.	Kreutzer's Jahresbericht der Photographie
Kristiania, Geogr. Selsk. Arb.	Det Norske Geografiske Selskabs Arbog
Kristiania, Norw. Mar. Investig. Rep.	Report on Norwegian Fishery and Marine Investigations
Kroyer, Naturhist. Tidssk.	Naturhistorisk Tidsskrift
Kühn-Archiv.	Kuhn-Archiv (formerly Berichte aus dem physiologischen Laboratorium und der Versuchsanstalt des Landwirtschaftlichen Instituts der Universitat Halle
Kult. Ing	Der Kultur-Ingenieur (F. Dunkelberg)
Kunst.	Kunstoffe
Lab. Club. Trans	Transactions of the Laboratory Club
Laboratory	The Laboratory
Laibach, Jahr. Gymnas.	Jahresbericht des k. k. Ober-Gymnasiums in Laibach
Laibach, Jahr. Realschule	Jahresbericht der k. k selbstandigen Unter-Realschule zu Laibach
Laibach, Jahresh.	Jahresheft des Vereins des Krainischen Landes Museums in Laibach
Laibach, Mus.-Ver. Krain Mitth.	Mittheilungen des Museal-Vereins fur Krain
Lancet	The Lancet, London
Landb. Cour	Landbouw-Courant
Landshut Bot. Ver. Ber.	Bericht des Botanischen Vereines in Landshut
Landw. Centr.	Landwirthschaftliches Centralblatt für Deutschland
Landw Jahr.	Landwirthschaftliche Jahrbucher Zeitschrift fur wissenschaftliche Landwirthschaft und Archiv des Koniglich Preussischen Landes-Oekonomie Kollegiums
Landw Jahr. Schweiz	Landwirtschaftliches Jahrbuch der Schweiz
Landw. Presse	Landwirtschaftliche Presse
Landw. Versuchs-Stat.	Die landwirthschaftlichen Versuchs-Stationen
Landw Ztg.	Landwirtschaftliche Zeitung
Laon, Soc Acad. Bull.	Bulletin de la Société Academique de Laon
Laurent Ann. Anat.	Annales Francaises et Etrangeres d'Anatomie et de Physiologie, appliquees a la Medecine et a l'Histoire Naturelle
Laurent Gerhardt, Compt. rend.	Comptes rendus Mensuels des Travaux Chemiques
Lausanne, Bull Soc Med.	Bulletin de la Société Medicale de la Suisse Romande
Lausanne, Bull. Soc Vaud.	Bulletin des Seances de la Société Vaudoise des Sciences Naturelles
Lausitz. Monatschr.	Lausitzische (und neue Lausitzische) Monatschrift Organ der Oberlausitzischen Gesellschaft der Wissen. schaften
Leather	Leather
Leather Mfr	Leather Manufacturer
Leather Tr. Rev.	Leather Trades Review
Leather World	Leather World, The
Lederind.	Lederindustrie (Deutsche Gerber-Zeitung)
Ledermarkt	Ledermarkt, Der. (See also Collegium)
Leeds, Trans. Phil. Soc	Transactions of the Philosophical and Literary Society of Leeds
Leicester, Lit. Phil Soc. Selection	Selection of Papers, of the Literary and Philosophical Society of Leicester
Leicester Soc Rep.	Leicester Literary and Philosophical Society . Report of the Council
Leicester Soc. Trans.	Transactions of the Leicester Literary and Philosophical Society

Leide	See Leyden
Leiiden, Ann. Acad.	Annales Academiae Lugduno-Batavae
Leiden, Tijdschr. Entom.	Tijdschrift voor Entomologie
Leipzig, Abh. Jablon. Ges.	Abhandlungen bei Begrundung der k. Sachsischen Gesellschaft der Wissenschaften am Tage der zweihundertjahrigen Geburtsfeier Leibnizens
Leipzig, Abh. Math. Phys.	*Abhandlungen der Mathematisch-Physischen Classe der Königlich Sächsischen Gesellschaft der Wissenschaften*
Leipzig, Arbeit. Physiol. Anst.	Arbeiten aus der physiologischen Anstalt zu Leipzig
Leipzig, Astron. Ges. Viertelj.	Vierteljahrsschrift der Astronomischen Gesellschaft
Leipzig, Ber. Math. Phys.	Berichte über die Verhandlungen (Math. Phys. Classe) der Königlich Sachsischen Gesellschaft der Wissenschaften zu Leipzig
Leipz. Färb. Ztg.	Leipziger Farber- und Zeugdrucker-Zeitung
Leipzig Jablon. Preisschr.	Preisschriften gekrönt und herausgegeben von der furstlich Jablonowski' schen Gesellschaft zu Leipzig
Leipzig, Monatschr. Text. Ind.	Leipziger Monatsschrift fur Textil Industrie
Leipzig, Naturf. Ges. Sitzber.	Sitzungsberichte der Naturforschenden Gesellschaft zu Leipzig
Leipzig, Physiol. Anst. Arb.	Arbeiten aus der Physiologischen Anstalt zu Leipzig
Leipzig, Schr. Naturf. Ges.	Schriften der Naturforschenden Gesellschaft zu Leipzig
Leipzig, Verh Med. Ges.	Verhandlungen der Medicinischen Gesellschaft
Leyden Mus. Notes	Notes from the Leyden Museum
Leo, Mag.	Magazin fur Heilkunde und Naturwissenschaft in Pohlen
Leoben, Berg. u. Hütt. Jahr.	Berg- und Huttenmannisches Jahrbuch der k. k. Montan. Lehranstalten zu Leoben und Pribram
Leonhard Bronn	See Neues Jahr. Mineral
Leonhard Bronn, Jahr.	Jahrbuch fur Mineralogie, Geognosie, Geologie, und Petrefaktenkunde
Leonhard Bronn, Neu. Jahr.	Neues Jahrbuch fur Mineralogie, Geognosie, Geologie und Petrefaktenkunde
Leonhard, Taschenbuch	Taschenbuch für die gesammte Mineralogie
Leonhard, Zts.	Zeitschrift fur Mineralogie
Leopold.-Carol. Deutsch. Akad. Naturf.	See Ac. Nat. Curios. Nova Acta. Leopoldina
Leopoldina	Leopoldina. Amtliches Organ der Kaiserlichen Leopoldino-Carolinischen Deutschen Akademie der Naturforscher
Letters on Brewing	Letters on Brewing
Les Mondes	Revue hebdomadaire des Sciences et de leurs application
Licht.	Licht: Zeitschrift fur Photographie: herausgegeben vom Photographischen Verein. zur Berlin
Liege, Ann. Acad.	Annales Academiae Leodiensis
Liege Assoc. Ingen. Annu.	See Rev. Univ. Mines
Liege, Mem. Soc. Emul.	Memoires de la Société Libre d'Émulation de Leiege
Liege, Mem. Soc. Sci.	Memoires de la Société (Royale) des Sciences de l'Agriculture, et des Arts a Liege
Leige Lab. Fredericq Trav.	Universite de Liege. Institut de Physiologie. Travaux du Laboratoire de Leon Fredericq
Lille Inst. Zool. Trav.	Travaux de l'Institut Zoologique de Lille et du Laboratoire de Zoologie Maritime de Wimereux (Pas-de-Calais). Travaux de la Station Zoologique de Wimereux

Lille Mem. Soc.	Memoires de la Société (Imperiale) des Sciences, de l'Agriculture et des Arts de Lille
Lille, Mem. Soc. Sci.	Memoires de la Société (Royale) des Sciences, etc , a Lille
Lille, Seances Publ.	Seances Publiques de la Société des Amateurs
Lille, Trav.	Recueil des Travaux de la Société d'Amateurs des Sciences, de l'Agriculture, et des Arts a Lille
Lille, Trav. Mem.	Travaux et Memoires de l'Universite de Lille
Lima, Mem. Cien. Nat.	Memorias de Ciencias Naturales y de Industrial (Lima)
Limbourg, Soc Sci. Bull	Bulletin de la Société Scientifique et Litteraire du Limbourg
Limoges, Assises	Assises scientifiques de Limoges (Institut des Provices de France)
Lindblom, Bot Notiser	Botaniska Notiser
Linn	Linnaea· ein Journal fur die Botanik
Linn. Entom.	Linnaea Entomologica
Linn. Soc. J.	The Journal of the Linnean Society. Botany and Zoology
Linn. Soc. Trans.	The Transactions of the Linnean Society of London
Linn. Soc Proc	Proceedings of the Linnean Society of London
Linneska Samf. Handl.	Linneska Samfundets Handlingar for ar 1832
Linz, Ber.	Bericht über das Museum Francisco-Carolinum in Linz
Lisboa, Acad. Sci. Mem	Historia e Memorias da Academia Real das Sciencias de Lisboa
Lisboa, Actas	Actas das Sessoes da Academia Real das Sciencias de Lisboa
Lisboa, Ann.	Annaes das Sciencias e Lettras
Lisboa, J Math Sci	Jornal de Sciencias Mathematicas, Physicas e Naturaes publicado sob os Auspicios da Academia Real das Sciencias de Lisboa
Litterar. Annal.	Litterarische Annalen der gesammten Heilkunde
Liverpool Biol. Soc. Proc	Proceedings and Transactions of the Liverpool Biological Society
Liverpool, Lit. Phil Soc. Proc.	Proceedings of the Literary and Philosophical Society of Liverpool
Liverpool Mar. Biol. Comm.	See Liverpool Biol Soc. Proc ; Liverpool Biol. Soc Proc. & Trans ; Liverpool Lit. Phil. Soc. Proc
Liverpool Med. Chir. J.	Liverpool Medico-Chirurgical Journal
Liverpool School Trop. Med. Mem.	Liverpool School of Tropical Medicine Memoirs
Liverpool, Thompson Yates Lab. Rep.	The Thompson Yates Laboratories Report
Loc. Gov. Bd. Rep. (Med. Off.)	.. Annual Report of the Local Government Board. Supplement containing the Reports of the Medical Officer
London	See Int. Congr. Hyg Trans , 1891; Int Congr Zool Proc. 1898
London, Ann. Med. Surg.	Annals of Medicine and Surgery, Records of the occurring Improvements, &c
London, Cryst. Soc. Proc	Proceedings of the Crystallological Society
London Elec Soc. Proc.	Proceedings of the London Electrical Society
London, Fed. Inst. Brewing J.	Journal of the Federated Institutes of Brewing containing the Transactions of the various Institutes
London J. Med.	London Journal of Medicine
London, Med. Phys. J.	The Medical and Physical Journal
London, Med. Soc. Trans.	Transactions of the Medical Society of London

London, Obstet. Soc. Trans.	Transactions of the Obstetrical Society of London
London, Odont. Soc Trans.	Transactions of the Odontological Society of London
London Path Soc Trans.	Transactions of the Pathological Society of London
Lond. Phot. Soc.	London Photographic Society
London Phys. Soc Proc.	Proceedings of the Physical Society of London
London Physiol. J.	London Physiological Journal
London Poly. Rev.	The London Polytechnic Review and Magazine
London, Poly. Mag	Polytechnic Magazine and Journal of Science, Letters, and Fine Arts
London, Sci Soc Proc.	Proceedings of the Scientific Society of London
London, Soc. Imp. Med Trans.	Transactions of the Society for the Improvement of Medical and Chirugical Knowledge
Lotos	Lotos, Jahrbuch fur Naturwissenschaft im Auftrage der Vereines "Lotos"
Lousiana Planter	Lousiana Planter and Sugar Maufacturer, The
Louvaine, Ann. Acad	Annales Academiae Lovaniensis
Lowell Obs Ann	Annals of the Lowell Observatory
Lucca, Atti Accad	Atti della R. Accademia Lucchese di Scienze, Lettere, et Arti
Lumière	La Lumière; Revue de la Photographie
Lumière elec	Lumière electrique, La
Lund, Acta Univ	Acta Universitatis Lundensis Lunds Iniversitets Ars-skrift. Afdelningen for Mathematik och Naturvetenskap
Lund Bot. For.	See Bot Centrbl ; Bot Notiser
Lund, Phys. Sallsk Tidskr	Physiografiska Sallskapets Tidskrift
Luneb., Denkschr	Denkschriften des naturwissenschaftlichen Vereins fur das Fusrtenthum Luneburg
Luneb., Jahr. Naturwiss Ver.	Jahresbericht uber die Thatigkeit des naturwissenschaftlichen Vereins in Luneburg
Luneb Jheft Naturwiss Ver.	Jahreshefte des Naturwissenschaftlichen Vereins fur das Furstentum Luneburg
Luxemb., Inst Roy Publ.	Publications de l'Institut Royal Grand-Ducal de Luxembourg Section des Sciences Naturelles
Luxemb P.	Luxembourg Patent
Luxemb Soc Bot. Rec Mem Trav	Recueil des Memoires et des Travaux publies par la Société Botanique du Grant-Duche de Luxembourg
Luxemb Soc. Sci Natur.	Société des Sciences Naturelles du Grand-Duche de Luxembourg
Lyon	Lyon scientifique et industriel
Lyon, Acad Sci. Mem.	Memoires de l'Academie des Sciences, Belles-Lettres, et Arts de Lyon
Lyon Mus. Hist Natur. Archiv.	Archives du Museum d'Histoire naturelle de Lyon
Lyon Soc Agric Ann.	Annales de la Société d'Agriculture, Histoire naturelle et Arts utiles de Lyon. Annales de la Société d'Agriculture, Sciences et Industrie de Lyon
Lyon Soc. Bot. Ann	Annales de la Société Botanique de Lyon
Lyon, Soc. Linn Ann.	Annales de Socétié Linneenne de la Lyon
Lyon, Soc. Linn. Compt rend	Comptes Rendus des Travaux de la Société de Medecine
Lyon, Soc Sci Med Mem	Memoires et Comptes-Rendus de la Société des Sciences Medicales de Lyon
Lyon Univ. Ann.	Annales de l'Universite de Lyon
Maandbl. Natuurweten.	Maandblad voor Natuurwetenschappen, uitgegeven door de Sectie voor Natuurwetenschappen van het Gennotschap ter Bevordering van Natuur-, Genees- en Heelkunde te Amsterdam

Maclurian Lyceum, Contrib	Contributions of the Maclurian Lyceum to the Arts and Sciences
Macon Acad Ann.	Annales de l'Academie de Macon Société des Arts, Sciences, Belles Lettres et (d')Agriculture (de Saone et-Loire)
Macon, Soc Agric Compt rend	Comptes Rendus des Travaux de la Société d'Agriculture, Sciences, et Belles-Lettres
Macon Soc Compt rend	Compte Rendu des Travaux de la Société (d'Agriculture), des Sciences, Arts et Belles lettres, de Macon
Madras J	The Madras Journal of Literature and Science
Madras Quart J	Madras Quarterly Journal of Medical Science
Madrid	See Congr. Int Hig. Act 1898
Madrid Acad Cien Mem.	Memories de la Real Academia de Ciencias Exactas, Fisicas y Naturales de Madrid
Madrid, Anales Hist Natur	Anales de Historia Natural
Madrid, Anales Minas	Anales de Minas
Madrid, Anuar	Anuario del Real Observatorio de Madrid
Madrid, Bol	Boletin Oficial del Ministerio de Comercio
Madrid, Ingen Ind Anales	Anales de la Asociacion de Ingenieros Industriales
Madrid, Mem	Memorias de la Real Academia de Ciencias
Madrid, Revista	Revista de los Progresos de las Ciencias exactas, fisicas, y naturales
Madrid, Soc Hist Natur Anales	Anales de la Sociedad Espanola de Historia Natural
Mag Gesammt Thierheilk	Magazin fur die gesammte Thierheilkunde
Mag Natur Hist	The Magazine of Natural History, and Journal of Zoology, Botany, Mineralogy, Geology, and Meteorology
Mag. Natur Phil	The Magazine of Natural Philosophy
Mag Naturvid	Magazin for Naturvidenskaberne
Mag Zool	Magasin de Zoologie
Magdeb V. Ver Abh. Naturwiss	Abhandlungen des Naturwissenschaftlichen Vereins zu Magdeburg
Magdeb V Ver. Festschr Naturwiss	Festschrift zur Feier des 25 jahrigen Stiftungstages des Naturwissenschaftlichen Vereins zu Magdeburg
Magdeb V. Ver Jahr Abh Naturwiss.	Jahresbericht und Abhandlungen des naturwissenshaftlichen Vereins in Magdeburg.
Magendie, J. Physiol	Journal de Physiologie, experimentale et pathologique
Magyar Akad Ertes. (Math Termesz)	Magyar Akademiai Ertesito A mathematikai, es Termeszettudomanyi osztalyok Kozlonye (Report of the Hungarian Academy. Communications of the Mathematical and Natural Science Sections)
Magyar Boripar	Magyar Boripar
Magyar Nemzeti Muzeum	See Termr. Fuz
Magyar Termt. Tars	See Termt Kozlon.
Magyar Tud Akad. Ertes.	A Magyar Tudomanyos Akademia Ertesitoje. (Report of the Hungarian Academy of Science) Akademiai Ertesito a Magyar Tud. Akademia Megbizasabol. (Report by the Committee of the Hungarian Academy of Science)
Magyar Tud. Akad. Ertek. (Math.)	Ertekezesek a Mathematikai Tudomanyok körebol. Kiadja a Magyar Tudomanyos Akademia. (Memoirs in the Mathematical Sciences. Published by the Hungarian Academy of Science)

Magyar Tud. Akad. Ertek. (Termt.)	Ertekezesek a Termeszettudomanyok körebol. Kiadja a Magyar Tudomanyos Akademia. (Memoirs in the Natural Sciences. Published by the Hungarian Academy of Science)
Magyar Tud Akad. Evk.	A Magyar Tudomanyos Akademia Evkonyvei. (Annals of the Hungarian Academy of Science)
Maine Loire Soc. Mem. Acad.	Memoires de la Société Academique de Maine et Loire
Majocchi, Ann Fis. Chim.	Annali di Fisica, Chimica, etc.
Malpighia	Malpighia. Rassegna mensuale di Botanica
Malta P.	Malta Patent
Malvern Field Club Trans.	The Transactions of the Malvern Naturalists' Club
Manufact. and Build.	The Manufacturer and Builder
Manchester, Engin. Proc.	Proceedings of the Manchester Institution of Engineers
Manchester, Lit. Phil. Soc Mem.	Memoirs of the Literary and Philosophical Society of Manchester
Manchester, Lit. Phil Soc. Proc.	Proceedings of the Literary and Philosophical Society of Manchester
Manchester Micro. Soc. Trans.	Manchester Microscopical Society. Transactions and Annual Report
Manchester, Owens Coll. Biol. Lab. Stud.	Studies from the Biological Laboratories of the Owens College
Manchester, Owens Coll. Stud. Biol.	Studies in Biology from the Biological Department of the Owens College
Mannheim, Jahr.	Jahresbericht des Mannheimer Vereins fur Naturkunde
Mans, Soc. Agric. Bull.	Bulletin de la Société d'Agriculture, etc , de la Sarthe
Mans, Soc. Bull.	Bulletin de la Société (Royale) d'Agriculture, Sciences et Arts du Mans
Mans, Soc. Roy. Trav.	Analyse des Travaux de la Société (Royale) des Arts du Mans
Marburg, Ges. Naturwiss. Schr.	Schriften der Gesellschaft zur Beforderung der gesammten Naturwissenschaften zu Marburg
Marianini	See Mem. Fis. Sperim.
Marne, Soc. Agric. Compte Annuel	Compte annuel et Sommaire des Travaux de la Société Agricole, etc., du departement de la Marne
Marne, Soc. Agric. Seance	Seance publique de la Société d'Agriculture, etc., du departement de la Marne
Marseille, Ann. Sci.	Annales de Sciences et de l'Industrie du midi de la France
Marseille Fac. Sci. Ann.	Annales de la Faculte des Sciences de Marseille
Marseille Lab. Zool. Mar. Trav.	See Marseille Mus. Ann.
Marseille, Mem. Acad.	Memoires publies par l'Academie de Marseille
Marseille, Mem. Soc. Emul.	Memoires de la Société d'Émulation de la Provence
Marseille Mus. Ann.	Annales du Musee d'Histoire naturelle de Marseille
Maschin.-Constr.	Der praktische Maschinen-Construkteur (W. Uhland)
Maschinenb.	Der Maschinenbauer
Mass. Bd. Health Report	Annual Report of the State Board of Health, Lunacy and Charity of Massachusetts. Annual Report of the State Board of Health of Massachusetts
Mass. Insects Report	. . .Annual Report on the Injurious and Beneficial Insects of Massachusetts
Mass. Med. Soc. Commun.	Massachusetts Medical Society's Communications
Mat. grasses	Le Matieres grasses
Maurice, Soc. Hist. Natur. Rapp.	Septieme Rapport Annuel sur les Travaux de la Société d'Histoire Naturelle de l'Lle Maurice

Mauritius, Meteorol. Soc. Proc.	Proceedings, &c, of the Meteorological Society of Mauritius
Mauritius, Meteorol. Soc. Trans.	Transactions of the Meteorological Society of Mauritius
Mauritius P.	Mauritius Patent
Mauritius Roy. Soc. Trans.	Transactions de la Société Royale des Arts et des Sciences de Maurice
Meaux, Bull. Soc. Archeol.	Bulletin de la Société d'Archeologie, Sciences, Lettres et Arts du dept de Seine et Marne
Mechan Engin. Inst. Proc.	Institution of Mechanical Engineers Proceedings
Meckel, Archiv.	Archiv fur Anatomie und Physiologie
Meckel, Deut. Archiv.	Deutsches Archiv. fur die Physiologie
Med. Assoc. J.	Journal edited for the Provincial Medical and Surgical Association
Med. Bot. Soc. Trans.	Transactions of the Medico Botanical Society of London
Med. Chem Unters	Medicinisch chemische Untersuchungen; aus dem Laboratorium fur angewandte Chemie zu Tubingen
Med. Chir Soc. Proc.	Proceedings of the Royal Medical and Chirurgical Society of London
Med.-Chir. Trans.	Medico-Chirurgical Transactions
Med. Chir Ztg.	Medicinisch-chirurgische Zeitung
Med Congr	See Congr Int Med C R, Congr. Int Sci. Med. C. T, Congr. Med Int Atti, Int. Med. Congr. Trans, Int Med Congr. Verh.
Med. Jahr.	Medizinische Jahrbucher, von der K. K. Gesellschaft in Wien
Med. Klinik.	Medizinische Klinik
Med. naturwiss. Archiv.	Medizinisch naturwissenschaftliches Archiv.
Med. Off. India Sci. Mem.	Scientific Memoirs by Medical Officers of the Army of India
Med. Phys J.	The Medical and Physical Journal
Med. Rec.	The Medical Record, N. Y.
Med. Times	The Medical Times, London
Med. Trans.	Medical Transactions
Med. Wochenschr.	Medizinische Wochenschrift
Med. Ztg Russ	Medicinische Zeitung Russlands
Medd. Gronland	Meddelelser om Gronland
Medd. K. Vetenskapsakad. Nobel-inst.	Meddelanden fran K. Vetenskapsakademiens Nobel-institut
Meisner, Ann.	Annalen der allgemeinen Schweizerischen Gesellschaft fur die gesammten Naturwissenschaften
Meisner, Anzeiger	Naturwissenschaftlicher Anzeiger der Allgemeinen Schweizerischen Gesellschaft fur die gesammten Naturwissenschaften
Melbourne	See Victoria
Mem. accad. Lincei	Memorie della r. accademia dei Lincei, Classe di scienze fisiche, mathematiche e naturali
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino
Mem. Chem. Soc.	Memoirs and proceedings of the Chemical Society of London prior to 1848
Mem. Coll. Sci. Eng. Kyoto	Memoirs of the College of Science and Engineering, Kyoto Imperial University
Mem. Fis. Sperim.	Memorie di Fisica sperimental
Mem. Imp. Mineral. Soc. Petrograd	Memoirs of the Imperial Mineralogical Society of Petrograd
Mem. Lepidopt., St. Petersb.	Memoires sur les Lepidopteres

Mem Manch. *Lit Phil.* Soc	*Memoirs and Proceeding* of the Manchester Literary and Philosophical Society
Mem Med. Milit.	Recueil de Memoires de Medecine, de Chirurgie et de Pharmacie Militaires
Mem poud. salp	Memorial des poudres et salpetres
Mem rev. soc cien "Antonio Alzate"	Memorias y revista de la sociedad cientifica "Antonio Alzate"
Mem. Soc Ing. civ	Memoires et Compte-Rendu des travaux de la Société des Ingenieurs Civils, etc
Mem. Soc Nat. Kiev	Memoirs of the Society Nat. Kiev.
Mem Valdarnesi	Memorie Valdarnesi
Mende, Soc. Agric Bull	Bulletin de la Société d'Agriculture, Industrie, Sciences, et Arts de departement de la Lozere
Mende, Soc Agric Mem	Memoires et Analyses des Travaux de la Société d'Agriculture, Commerce, Sciences, et Arts de la ville de Mende, departement de la Lozere
Merck's Ann Rep	Merck's Annual Report
Merck's Archiv	Merck's Archives, New York
Messenger Math	The Messenger of Mathematics
Met.	Metallurgical-Metallurgia
Met. Chem Eng	Metallurgical and Chemical Engineering
Met ital.	Metallurgia italiana, La
Met. Rev.	The Metallurgical Review
Metal Ind	The Metal Industry
Metal Tech	Metal Technik
Metall Ind. Ztg	Deutsche Metall-Industrie Zeitung
Metallarb.	Der Metallarbeiter
Metallurgie	Metallurgie
Metaxa, Ann Med. Chir	Annali medico chirurgici.
Metz Acad. Mem	Memoires de l'Academie (Imperiale) de Metz
Metz, Assises	Assises scientifiques de Metz (Institut des Provinces de France)
Metz, Seance Gen	Société des Lettres, Sciences, Arts, et Agriculture de Metz
Metz Soc. Hist Natur Bull.	Bulletin de la Société d'Histoire naturelle de Metz
Mex.	Mexican, Mexico, Mexicane
Mex. P	Mexican Patent
Mex. Mus Anales	Anales del Museo Nacional de Mexico
Mex Registro Trim	Registro trimestre, o Coleccion de Memorias de Historia, Literatura, Ciencias, etc, por una Sociedad de Literatos
Mex Soc "Alzate" Mem.	Memorias de la Sociedad Cientifica "Antonio Alzate"
Mexique Archiv. Comm. Sci.	Archives de la Commission Scientifique du Mexique, publiees sous les auspices du Ministere de l'Instruction Publique
Meyer Bros Drug	Meyer Brothers Druggist, St. Louis
Meyer Jahr Chem	R. Meyer's Jahrbuch der Chemie
Michigan, Fish Comm Report	Biennial Report of the State Board of Fish Commissioners. (Contains the Michigan Fish Comm. Bull)
Micro J.	Quarterly Journal of Microscopical Science
Micro Soc. J.	Journal of the Royal Microscopical Society
Micro Soc. Trans	Transactions of the Microscopical Society of London
Midl. Drug	Midland Druggist and Pharmaceutical Review
Midl. Med. Surg Rep	Midland Medical and Surgical Reporter
Midl. Quart. J. Med Sci.	The Midland Quarterly Journal of Medical Sciences
Milano, Ann. Scienz.	Annali di Scienze e Lettere

Milano, Atti Ginnas	Atti dell' I R Ginnasio Liceale Convitto Longone in Milano
Milano, Atti Ist Lomb	Atti dell' I R Istituto Lombardo di Scienze, Lettere, ed Arti
Milano, Atti Soc. Ital	Atti della Societa Italiana di Scienze Naturali
Milano, Cagnola Atti	Atti della Fondazione Scientifica Cagnola dalla sua istituzione in poi
Milano, Giorn Soc Incor	Giornale della Societa d'Incoraggiamento delle Scienze, etc , stabilita in Milano
Milano, Ist. Lomb Adunanze	Solenni Adunanze del R Istituto Lombardo di Scienze e Lettere
Milano, Ist Lomb Rapporti	Rapporti sui Progressi delle Scienze del R Istituto Lombardo di Scienze
Milano, Ist Lomb Rend	Rendiconti dell' Istituto Lombardo di Scienze e Lettere —Classe di Scienze matematiche e naturali
Milano, Mem Ist Lomb	Memorie dell' I R Istituto Lombardo di Scienze, etc
Milano, Mem Ist Lomb Veneto	Memorie dell' I R Istituto del regno Lombardo-Veneto
Milch Zentr	Milchwirtschaftliches Zentralblatt
Milch Ztg	Milch Zeitung
Min Eng World	Mining and Engineering World
Min. J	The Mining Journal
Min Rev	Mining Review, a Monthly Record of Geology
Min Sci	Mining Science
Min Sci Press	Mining and Scientific Press
Min Smelt Mag	The Mining and Smelting Magazine a monthly review of Practical Mining, Quarrying, and Metallurgy
Min Soc. J	See Min Mag
Mineral Mag	The Mineralogical Magazine and Journal of the Mineralogical Society of Great Britain and Ireland
Mineral Mitth	Mineralogische Mittheilungen
Mineral Petr Mitth	(Tschermak's) Mineralogische und Petrographische Mittheilungen
Mines and Minerals	Mines and Minerals
Minn Acad Sci Bull	Bulletins of the Minnesota Academy of Natural Sciences
Minn Acad Sci Pap	The Minnesota Academy of Natural Sciences at Minneapolis, Minn Occasional Papers
Minn. Bot Stud	Geological and Natural History Survey of Minnesota. Minnesota Botanical Studies
Miquel, Bull	Bulletin des Sciences Physiques et Naturelles en Neerlande
Misc. Ent	Miscellanea Entomologica
Mitau, Quatember	Die Quatember
Mitth Artil Geniew	Mittheilungen uber Gegenstande des Artillerie und Genie-wesens
Mitth. Bohmen Archit Ing Ver.	Mittheilungen des Architekten und Ingenieur Vereins im Konigreiche Bohmen
Mitth Centralst Wiss-tech Unters.	Mittheilungen aus der Centralstelle fur wissenschaftlichtechnische Untersuchungen
Mitth. Gewerbever Nassau	Mittheilungen fur den Gewerbeverein fur Nassau
Mitth Kais. Gesundhts	Mittheilungen aus dem Kaiserlichen Gesundheitsamte, Berlin
Mitth Konigl. Materialprufungsamt	Mitteilungen aus dem Koniglichen Material prufungsamt zu Gross Lichterfelde West
Mitth Hannov. Gewerbever	Mittheilungen des Gewerbevereins fur Hannover

Mitth. Lebensm. Hyg.	Mitteilungen aus dem Gebiete der Lebensmitteluntersuchung und Hygiene veröffentlicht vom Schweizer Gesundheitsamt
Mitth. Malerei	Technische Mitteilungen für Malerei
Mitth. konig. Prüfungsans Wasser-versorgung	Mitteilungen aus der königlichen Prufungsanstalt für Wasser-versorgung und Abwasser beseitung zu Berlin
Mitth. Tech. Gew Mus.	Mitteilungen aus dem Technischen Gewerbe Museum
Mitth. Techn. Versuchsamtes	Mittheilungen des k. k. Technischen Versuchsamtes
Mitth. Zool. Sta. Neapel	Mittheilungen aus der zoologischen Station zu Neapel. etc.
Mo Insects Report	Annual Report on the Noxious, Beneficial and other Insects, of the State of Missouri, made to the State Board of Agriculture
Mod. Sugar Planter	Model Sugar Planter, The
Modena, Accad. Sci. Mem.	Memorie della Regia Accademia di Scienze, Lettere ed Arti di Modena
Modena, Annu. Soc Natur.	Annuario della Societa dei Naturalisti in Modena
Modena Atti Soc. Natur.	Atti della Societa dei Naturalisti di Modena
Modena, Mem Soc. Ital	Memorie di Matematica e di Fisica della Societa Italiana delle Scienze
Modena, Relazione	Relazione delle Adunanze della R. Accademia di Scienze, Lettere, ed Arti di Modena, nell' Anno Academico 1812–43
Moigno, Annu. Cosmos	Annuaire du Cosmos
Mois chim. electrochim.	Mois chimique et electrochimique, Le
Mois min. met.	Mois minier et metallurgique, Le
Mois sci. ind.	Mois scientifique et industriel, Le
Moleschott, Unters	Untersuchungen zur Naturlehre des Menschen und der Thiere
Moll, Ann	Annalen der Berg- und Huttenkunde
Moll, Efemeriden	Efemeriden der Berg- und Huttenkunde
Moll, Jahr. Berg.	Jahrbucher der Berg- und Huttenkunde
Moll, Neue Jahr.	Neue Jahrbucher der Berg und Huttenkunde
Mon. ceram verr.	Moniteur de la ceramique de la verrerie et journal du ceramiste et du chaufournier (reunis)
Mon. cord.	Moniteur de la cordonnerie
Mon. fils. tiss.	Moniteur des fils et tissus
Mon Ind.	Moniteur Industriel
Mon. Ind Belge	Moniteur Industriel Belge
Mon. Pap.	Moniteur Papeterie
Mon. Sci	Moniteur Scientifique (Quesneville)
Mon. teint.	Moniteur de la teinture des apprets et de l'impression des tissus
Monats.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften. Gesammelte Abbhandlungen aus den Sitzungsberichten der kaiserlichen Akademie der Wissenschaften
Monats Dermatol.	Monatshefte fur praktische Dermatologie
Monatsbl. Hannover Gewerbever.	Monatsblatt des Gewerbevereins fur Hanover
Monatschr. Text.-Ind.	Leipziger Monatsschrift fur Textil-Industrie
Monatschr. Zahn.	Monatschrift fur Zahnärzte
Montevideo Mus. Nac. Anales	Anales del Museo Nacional de Montevideo
Monthly Amer. J. Geol.	Tne monthly Journal of Geology and Natural Science
Monthly Archiv. Med Sci.	Monthly Archives of the Medical Sciences

Monthly Cons. & Trade Report	The monthly Consular and Trade Reports
Montpellier, Acad. Proces-Verb.	Extraits des Proces-Verbaux des Seances de l'Academie des Sciences et Lettres
Montpellier, Acad. Sci. Mem.	Academie des Sciences et Lettres de Montpellier
Montpellier Inst. Zool. Trav.	Travaux originaux du Laboratoire Zoolique de la Faculte des Sciences de Montpellier et de la Station Maritime de Cette
Montpellier, Mem. Acad. Sect. Med.	Memoires de l'Academie des Sciences et Lettres Section de la Medecine
Montpellier, Recueil. Bull.	Recueil des Bulletins publies par la Société Libre des Sciences, etc.
Montreal Natur. Hist. Soc. Proc.	See Canad. Rec. Sci.
Montreal Pharm. J.	Montreal Pharmaceutical Journal
Montsouris	See under Paris
Morphol. Arb.	Morphologische Arbeiten
Morphol. Jahr.	Morphologisches Jahrbuch
Moscou	See Congr Int Anthrop C. R 1892, Congr Int. Med C R. 1897, Congr Int Zool (C R) 1892
Moscou, Comment. Soc. Phys. Med.	Commentationes Societatis Physico Medicae apud Universitatem Mosquensem institutae
Moscou, Soc. Natur. Bull.	Bulletin de la Société Imperiale des Naturalistes
Moscou, Soc. Natur. Mem.	Memoires de la Société Imperiale des Naturalistes de Moscou
Moscou, Soc. Natur. Nouv. Mem.	Nouveaux Memoires de la Société Imperiale des Naturalistes de Moscou
Moscow Soc. Sci. Bull.	Bulletin of the Imperial Society of Lovers of Natural Science, Anthropology and Ethnography, in connection with the Imperial University of Moscow
Moscow Univ. Mem. (Natur. Hist)	Scientific Memoirs of the Imperial University of Moscow. Natural History Section
Moscow Univ. Mem. (Phys.-Math.)	Scientific Memoirs of the Imperial University of Moscow Physico-Mathematical Section
Moselle, Bull. Soc. Hist. Natur.	Bulletin de la Société d'Histoire Naturelle du departement de la Moselle
Moselle, Trav. Soc. Sci. Med.	Expose des Travaux de la Société des Sciences Medicales de la Moselle
Mov. Pict. World	Moving Picture World
Mulder, Archief.	Natuur- en Scheikundig Archief
Mulder, Scheik. Verh.	Scheikundige Verhandelingen en Onderzoekingen
Müller, Archiv.	Archiv. fur Anatomie, Physiologie, und wissenschaftliche Medicin.
München, Akad. Abh.	Abhandlungen der Mathematisch-Physikalisch Classe der koniglich Bayerischen Akademie der Wissenschaften
München, Akad. Sitzber.	Sitzungsberichte der Mathematisch-Physikalischen Classe der k. B. Akademie der Wissenschaften Munchen
München Bot. Ver.	See Bot Centrbl.
München, Bull. Akad.	Bulletin der k. Akademie der Wissenschaften
München, Denkschr.	Denkschriften der Kongl Baierischen Akademie der Wissenschaften zu Munchen
München, Entom. Ver. Mitth.	Mittheilungen des Munchener Entomologischen Vereins
München, Gelehrte Anz.	Gelehrte Anzeigen

Munchen Ges. Morphol. Physiol. Sitzber	Sitzungsberichte der Gesellschaft fur Morphologie und Physiologie in München
Munchen, Naturwiss. Tech. Comm Abh	Abhandlungen der naturwissenschaftlichtechnischen Commission bei der Konigl. Baierischen Akademie
Munchen Phot Ges	See Wien, Photogr. Correspond.
Munchen, Sitzber.	Sitzungsberichte der Konigl. Baierischen Akademie der Wissenschaften zu Munchen
Munchen Thierarznei-Schule Jahr.	Jahresbericht der k. Central-Thierarznei-Schule in Munchen
Munchen Thierarztl. Hochschule Jahr.	Jahresbericht der k Thierärztlichen Hochschule in Munchen
Munchen, Zts Archit.	Zeitschrift des Bayerischen Architekten- und Ingenieur-Vereins
Munic Engin	Municipal Engineer
Munic. J Engin	Municipal Journal and Engineer
Munster, Abh Aerzt Ges.	Abhandlungen und Beobachtungen der arztlichen Gesellschaft zu Munster
Museum Senckenb	Museum Senckenbergianum
Must. Ztg.	Leipziger Farber Zeitung (Farberei Musterzeitung)
N. Brunsw. Natur. Hist Soc Bull.	Bulletin of the Natural History Society of New Brunswick
N. England Bot Club	See Rhodora
N Engl Eng.	New England Engineer, The
N. England J. Med.	New England Journal of Medicine and Surgery
N Erf Erfahr.	Neuste Erfindungen und Erfahrungen
N Hampshire San Bull	New Hampshire Sanitary Bulletin
N. Haven.	See Connecticut
N Idea	New Idea (The), Detroit
N. Med. Phys J	New Medical and Physical Journal
N. Mex Agric Coll Bull.	New Mexico Agricultural College. Experiment Station. Las Cruces, N. M Bulletin New Mexico College of Agriculture and the Mechanic Arts Agricultural Experimental Station Bulletin
N. Orleans Med Surg J.	New Orleans Medical and Surgical Journal
N. Orleans Proc.	Proceedings of the New Orleans Academy of Sciences
N. Russ Soc Natur Mem.	Memoirs of the New Russian Society of Naturalists
N. S. Wales, Acclim. Soc. Report	Annual Reports (3, 6, and 7) of the Acclimatisation Society of N. S W
N S. Wales Dept Mines Report	Annual Report of the Department of Mines (and Agriculture), New South Wales
N S. Wales, Entom. Soc Trans	The Transactions of the Entomological Society of New South Wales
N. S. Wales Linn Soc. (Macleay Mem. Vol)	Linnean Society of New South Wales. The Macleay Memorial Volume
N. S. Wales, Linn. Soc. Proc.	The Proceedings of the Linnean Society of New South Wales
N. S. Wales P.	New South Wales Patent
N. S. Wales, Phil. Soc. Trans.	Transactions of the Philosophical Society of New South Wales
N. S. Wales, Roy. Soc. J.	Journal and Proceedings of the Royal Society of New South Wales
N S. Wales, Roy. Soc. Trans.	Transactions of the Royal Society of New South Wales
N. Y. Acad. Ann.	Annals of the New York Academy of Sciences, late Lyceum of Natural History
N. Y. Acad. Mem.	New York Academy of Sciences. Memoirs
N. Y Acad Trans	Transactions of the New York Academy of Sciences

N. Y. Acad. Med. Bull.	Bulletin of the New York Academy of Medicine
N. Y. Acad. Med. Trans.	Transactions of the New York Academy of Medicine
N. Y. Agric. Soc. Trans.	Transactions of the New York State Agricultural Society
N. Y. Bot. Club Bull.	Bulletin of the Torrey Botanical Club
N. Y. Entom. Soc. J.	Journal of the New York Entomological Society
N. Y. Insects Report	Report on the Noxious, Beneficial and other Insects of the State of New York
N. Y. J. Med.	New York Journal of Medicine and the Collateral Sciences
N. Y. Linn. Soc. Trans.	Transactions of the Linnaean Society of New York
N. Y. Lit. Phil. Soc. Trans.	Transactions of the Literary and Philosophical Society of New York
N. Y. Lyceum Ann	Annals of the Lyceum of Natural History of New York
N. Y. Lyceum, Proc.	Proceedings of the Lyceum of Natural History in the City of New York
N. Y. Med. J.	New York Medical Journal
N. Y. Med Repos	Medical Repository of New York
N. Y. Med. Soc. Trans	Transactions of the Medical Society of the State of New York
N. Y. Mus Bull.	University of the State of New York Bulletin of the New York State Museum
N. Y. Mus. Mem.	Memoirs of the New York State Museum
N. Zeal. Inst. Trans.	Transactions and Proceedings of the New Zealand Institute
N. Zeal. Inst Min Engin Trans	Transactions of the New Zealand Institute of Mining Engineers
N. Zeal. J. Sci	The New Zealand Journal of Science
N. Zeal. P.	New Zealand Patent
N. Zeal Pap & Rep	New Zealand Papers and Reports relating to Minerals and Mining
Nachr. könig Ges	Nachrichten von der koniglichen Gesellschaft der Wissenschaften zu Gottingen (Mathematische-physikalische Klasse)
Nancy, Acad. Stanislas Mem.	Academie de Stanislas Memoires de la Société (Royale) des Sciences, etc , de Nancy
Nancy Soc Sci Bull.	Bulletin de la Société des Sciences de Nancy
Nancy Soc. Sci. Mem	Memoires de la Société (Royale) des Sciences, Lettres, et Arts de Nancy
Nancy Soc. Sci. Trav.	Precis analytique des Travaux de la Société (Royale) des Sciences, Arts, et Agriculture de Nancy
Nantes J. Med.	Journal de la Section de Medecine de la Société Academique du departement de la Loire Inferieure
Nantes, Ann. Soc. Acad	Annales de la Société Academique de Nantes et du departement de la Loire Inferieure
Nantes Soc. Sci Natur Bull	Bulletin de la Société des Sciences naturelles de l'Ouest de la France
Napoli Accad. Aspir. Ann	Annali della Accademia degli aspiranti Naturalisti
Napoli Accad. Atti	Atti della Reale Accademia delle Scienze Fisiche e Matematiche
Napoli Accad. Pontan. Atti	Atti dell' Accademia Pontaniana
Napoli Accad. Sci Atti	Atti della Reale Accademia della Scienze e Belle Lettere; Sezione della Societa R. Borbonica
Napoli Accad. Sci. Mem.	Memorie della R. Accademia della Scienze
Napoli Giorn. Mat.	See Giornale di Matemat.
Napoli, Atti Ist. Incorr.	Atti del Real Istituto d'Incorraggiamento alle Scienze Naturali di Napoli

Napoli Lucifero	Il Lucifero
Napoli Mus.	Museo di Letteratura e Filosofia
Napoli, Ann. Mus. Zool.	Annuario del Museo Zoologico della R. Universita di Napoli
Napoli Rend.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche. (Sezione della Societa Reale di Napoli)
Napoli Soc. Natur. Boll.	Bollettino della Societa di Naturalisti in Napoli
Natl. Assoc. Retail Drug. Notes	The Journal of the National Association of Retail Druggists, Chicago
Natl. Disp.	National Dispensatory
Natl. Drug.	National Druggist
Natl. Eclect. Med. Assoc. Quart.	The National Eclectic Medical Association Quarterly, Cincinnati
Natl Glass Budget	National Glass Budget
Natl. Inst. Bull.	Bulletin of the Proceedings of the National Institution for the Promotion of Science
Natur. Can.	Le Naturaliste Canadien. Bulletin de Recherches, Observations et Decouvertes se rapportant a l'Histoire naturelle du Canada
Natur. Sicil.	Il Naturalista Siciliano. Giornale di Scienze Naturali
Natur. J.	The Naturalists' Journal
Naturaleza	La Naturaleza. Periodico cientifico de la Sociedad Mexicana de Historia Natural
Naturalist (Yorks)	The Naturalist: Journal of the West Riding Consolidated Naturalists' Society
Naturaliste	Le Naturaliste
Nature	Nature
Naturf.	Der Naturforscher
Natur. Hist. Review	The Natural History Review and Quarterly Journal of Science
Naturhist. Notizen	Naturhistorische und chemisch-technische Notizen nach den neuesten Erfahrungen
Naturhist. Tidsskr.	Naturhistorisk Tidsskrift
Naturwiss. Umschau Chem. Ztg.	Naturwissenschaftliche Umschau der Chemiker-Zeitung
Natuurk Tijdschr.	Natuurkundige Tijdschrift, inhoudende Phijsica, Chemie, Pharmacie, Nat. Hist, &c., uitg. van wege het Genootschap: "Tot nut en vergenoegen," te Arnhem.
Nauche, J. Galvan.	Journal du Galvanisme, de Vaccine, etc.
Naval Archit. Trans.	Transactions of the Institution of Naval Architects
Naval Sci.	Naval Science: a Quarterly Magazine for promoting the improvement of Naval Architecture, Marine Engineering, Steam Navigation, and Seamanship
Neapel Zool. Sta, Fauna & Flora	Fauna und Flora des Golfes von Neapel und der angrenzenden Meeres-Abschnitte herausgegeben von der Zoologischen Station zu Neapel
Neapel Zool. Sta. Mitth.	Mittheilungen aus der Zoologischen Station zu Neapel
Nebraska Univ. Stud.	University Studies. Published by the University of Nebraska
Nederl Archiv.	See Selenka
Nederl. Archief Natuurk.	Nederlandsch Archief voor Genees-en Natuurkunde
Nederl. Bot Ver. Versl. en Meded.	See Nederl. Kruidk. Arch.
Nederl. Dierk. Ver. Tijdschr.	Tijdschrift der Nederlandsche Dierkundige Vereeniging
Nederl. Entom Ver.	See Tijdschr. Ent.

Nederl. Kruidk. Archief.	Nederlandsch Kruidkundig Archief
Nederl. Lancet	Nederlandsch Lancet. Tijdschrift aan de praktische Chirurgie, etc
Nederl. Tijdschr. Dierkunde	Nederlandsch Tijdschrift voor de Dierkunde, uitgegeven door het koninklijk Zoologisch Genootschap Natura Artis Magistra te Amsterdam
Nederl. Tijdschr. Geneesk.	Nederlandsch Tijdschrift voor Geneeskunde, tevens orgaan der Nederlandsche Maatschappij tot de Bevordering der Geneeskunst
Neuchatel Soc. Sci. Bull.	Bulletin de la Société des Sciences Naturelles de Neuchatel
Neues Bergmänn J.	Neues bergmannisches Journal
Neues Jahr. Min.	Neues Jahrbuch fur Mineralogie, Geologie und Palaeontologie
Neues Lausitz. Mag.	Neues Lausitzisches Magazin; unter Mitwirkung der Oberlausitzischen Gesellschaft der Wissenschaften
Neue med.-chir. Ztg.	Neue medicinisch-chirurgische Zeitung
Neues Nord. Archiv.	Neues nordisches Archif fur Natur und Arzneikunde, verfasst von einer Gesellschaft nordischer Gelehrten
Neue Preuss. Provinz. Blatt.	Neue Preussische Privinzial-Blatter
Neu-Vorpommern Mitth.	Mittheilungen aus dem naturwissenschaftlichen Vereins fur Neu-Vorpommern und Rugen in Greifswald
Newbury Field Club Trans.	Transactions of the Newbury District Field Club
Newcastle Chem. Soc. Trans.	Newcastle-upon-Tyne Chemical Society Transactions
Newf. P.	Newfoundland Patent
Newman. Entom.	The Entomologist
Newport Natur. Hist. Soc. Proc.	Proceedings of the Newport Natural History Society
Nicholson J.	Journal of Natural Philosophy, Chemistry, and the Arts
Nick.	The Nickelodeon
Niederl Archiv. Zool.	Niederlandisches Archiv. fur Zoologie
Niederosterr. Gewerb-Ver. Verh.	Verhandlungen des Niederösterreichischen Gewerbe-Vereins
Niederrhein. Ges. Naturk. Sitzber.	Sitzungsberichte der Niederrheinischen Gesellschaft fur Natur- und Heilkunde zu Bonn
Niederrhein. Ges. Organ.	Organ fur die gesammte Heilkunde; herausgegeben von der Niederrheinischen Gesellschaft fur Natur- und Heilkunde zu Bonn
Nieuw Archief Wisk.	Nieuw Archief voor Wiskunde
Nimes Soc. Sci. Bull.	Bulletin de la Société d'Etude des Sciences Naturelles de Nimes
Nor. Amer. Med. Chir. Rev.	The North-American Medico-Chirurgical Review
Nor. Eng. Inst. Min. Engin. Trans.	North of England Institute of Mining and Mechanical Engineers. Transactions
Nor. Staff. Field Club Rep.	(The) North Staffordshire (Naturalists') Field Club (and Archaeological Society). Annual Report (and Transactions)
Nord. Braband, Handel. prov. Genoots.	Handelingen van het provinciaal Genootschap van Kunsten en Wetenschappen in Nord Braband
Nord France Soc. Linn. Bull.	Bulletin de la Société Linneenne du Nord de la France
Nord France Soc. Linn. Mem.	Memoires de la Société Linneenne du Nord de la France

Nord, Mem. Soc. Agric.	See Douai
Nord, Soc. Agric. Seance Publ.	Seance Publique de la Société d'Agriculture, Sciences, et Arts, etc., du departement du Nord
Nordamerik. Monatsber.	Nordamerikanischer Monatsbericht fur Natur- und Heilkunde
Norddeut. Landwirth	Der norddeutsche Landwirth
Nordisches Archiv.	Nordisches (u. Neues Nordisches) Archiv. für Naturkunde und Arzneiwissenschaft
Norf. Norw. Natur. Soc. Trans.	Transactions of the Norfolk and Norwich Naturalists' Society
Normandie	See Caen
Normandie Soc. Linn. Bull.	Bulletin de la Société Linneenne de Normandie
Normandie Soc Linn. Mem.	Memoires de la Société Linneenne de Normandie
Normandie Soc. Linn. Seance Publ.	Seance Publiques de la Société Linneenne de Normandie
Norsk Tidsk. Vid Litt.	Norsk Tidskrift for Videnskab og Litteratur.
Norske Videnskab. Skrift.	Det Kongelige Norske Videnskabersselskabs Skrifter i det 19 de Aarhundrede
Northampton Natur. Hist Soc. J.	Journal of the Northampton(shire) Natural History Society and Field Club
Northern J. Med.	Northern Journal of Medicine
Northumb. Natur. Hist Soc. Trans.	Transactions of the Natural History Society of Northumberland, Durham, and Newcastle-upon-Tyne
Northwestern Drug.	Northwestern Druggist (The), Minneapolis
Norw. P.	Norwegian Patent
Notarisia	Notarisia. Commentarium Phycologicum. La Notarisia. Commentario Ficologico Generale. Parte speciale della Rivista Neptunia
Notices of Judgment, U. S Dept. Agric	Notices of Judgment, U. S. Department of Agriculture
Notiz Archit. Ver. Niederrhein	Notizblatt des Architekten und Ingenieur Vereins fur Niederrhein und Westfalen
Notiz. Riga	Notizblatt des technischen Vereins zu Riga
Nouv. Ann. Math.	Nouvelles Annales de Mathematiques
Nouv. Archiv. Miss Sci.	Nouvelles Archives des Missions Scientifiques et Litteraires
Nouv. remedes	Nouveaux remedes, Paris
Nova Acta Acad. Nat. Curios.	Novorum Actorum Academiae Caesareae Leopoldino Carolinae Germanicae Naturae Curiosorum
Nova Scotia Inst. Sci Proc. & Trans.	(The) Proceedings and Transactions of the Nov Scotian Institute of (Natural) Science
Nova Scotia, Trans. Lit. Sci. Soc.	Transactions of the Literary and Scientific Society o Nova Scotia
Novitates Zool.	Novitates Zoologicae. A Journal of Zoology i connection with the Tring Museum
Nuov. Ann. Sci. Natur.	Nuovi Annali delle Scienze naturali
Nuov. Antol. Sci.	Nuova Antologia di Scienze, Lettere (Lettere. Scienze ed Arti
Nuov. Cimento	Il Nuovo Cimento, Giornale di Fisica, di Chimica, di Storia Naturale
Nuov. Giorn. Bot. Ital	Nuovo Giornale Botanico Italiano (e Bullettino dell Societa Botanica Italiana)
Nuov. Notarisia	La Nuova Notarisia. Rassegna (trimestrale) co sacrata allo Studio delle Alghe (e Corollario al "Sylloge Algarum Omnium")
Nürnb. Natur. Ges. Abh.	Abhandlungen der Naturhistorischen Gesellschaft z Nurnberg
Nye Hygaea	Nye Hygaea

Nyt Mag. Naturvid.	Nyt Magazin for Naturvidenskaberne
Nyt Tidsskr. Fys. Kem.	Nyt Tidsskrift for Fysik og Kemi
Oberhess. Ges. Ber.	Berichte der Oberhessischen Gesellschaft für Natur- kunde und Heilkunde in Giessen
Odontol Soc Trans	Transactions of the Odontological Society of Great Britain
Oesterr Bot Zts.	Oesterreichische Botanische Zeitschrift
Oesterr. Chem. Ztg.	Oesterreichische Chemiker Zeitung
Oesterr. landw. Wochenbl.	Oesterreichisches landwirtschaftliches Wochenblatt
Oesterr. Med Jahr	Medicinisches Jahrbuch des k. k Oesterreichischen Staates
Oesterr Med Wochenschr.	Oesterreichische Medicinische Wochenschrift, als Erganzungsblatt der medicinischen Jahrbücher
Oesterr. Wochenschr.	Oesterreichische Wochenschrift fur Wissenschaft, Kunst, und offentliches Leben
Oesterr. Zts Berg Huttenw.	Oesterreichische Zeitschrift fur Berg- und Huttenwesen
Oesterr. ung Zts. Zuckerind.	Oesterreichisch ungarische Zeitschrift fur Zuckerindustrie und Landwirtschaft
Off. Gaz	Official Gazette, United States Patent Office
Offenbach. Ver. Naturk. Ber.	Bericht des Offenbacher Vereins fur Naturkunde uber seine Thätigkeit
Oil Colour J.	Oil and Colourman's Trade Journal
Oil, Paint Drug Rep	Oil, Paint and Drug Reporter
Oise	See Beauvais
Oise Mem. Soc Acad.	Memoires de la Société Academique d'Archeologie, Sciences, et Arts du departement de l'Oise
Oken Isis	Isis, oder Encyclopadische Zeitung
Omaha Drug	Omaha Druggist (The), Omaha
Omodei Ann Univ.	Annali Universali di Medicina
Ontario Entom. Soc Rep	Report of the Entomological Society of Ontario
Oporto	See Porto
Ophthalm Bibliothek	Ophthalmologische Bibliothek
Ophthalm. Hosp Reports	Ophthalmic Hospital Reports and Journal of the Royal London Ophthalmic Hospital
Ophthalmic Rev.	The Ophthalmic Review, a Quarterly Journal of Ophthalmic Surgery and Science
Organ Rübenzuckerind	Organ des Centralvereins fur Rubenzuckerindustrie
Orgelb	Die Orgelbauzeitung
Orleans Ann	Annales de la Société Royale des Sciences, Belles-Lettres, et Arts d'Orleans
Orleans, Bull.	Bulletin des Sciences Physiques, Medicales, et d'Agriculture d'Orleans
Ornis	Ornis, oder das Neuste und Wichtigste der Vogelkunde, etc
Ornith Jahr.	Ornithologisches Jahrbuch
Ornith Monatsber.	Ornithologische Monatsberichte
Ornithol.	The Ornithologist
Ornithol Ool	The Ornithologist and Oologist
Örsted Tidsskrift	Tidsskrift for Naturvidenskaberne
Orvos-Termesz Ertes	Orvos-Termeszettudomanyi Ertesito a Kolozsvari Orvos-Termeszettudomanyi Tarsulat es az Erdelyi Museum-Egylet Termeszettudomanyi Szakosztalyanak az .szakuleseiröl .(Medical and Natural History Proceedings of the sections of the Klausenburg Medical and Natural History Society and of the Natural History section of the Museum Association of Transylvania

Osnabrück, Jahr.	Jahresbericht des Naturwissenschaftlichen Vereins zu Osnabrück
Ottawa Field-Natur. Club Trans.	Ottawa Field-Naturalists' Club Transactions
Ottawa Natur.	The Ottawa Naturalist
Ouest France Soc. Sci. Nat. Bull.	See Nantes...
Oversigt K. Danske Vidensk. Selsk. Forh.	Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlinger
Pacific Drug. Rev.	Pacific Drug Review, Portland
Pacific Pharm.	Pacific Pharmacist
Padova, Mem. Acad.	Memorie dell' Accademia di Scienze, Lettere, ed Arti di Padova
Padova, Nuovi Saggi	Nuovi Saggi dell' Accademia di Scienze, Lettere, ed Arti di Padova
Padova, Rivista Period	Rivista Periodica dei Lavori della I. R. Accademia di Scienze, Lettere, ed Arti di Padova
Padova, Soc. Sci. Atti	Atti della Societa Veneto-Trentina di Scienze naturali
Padova Soc. Sci. Bull.	Bullettino della Societa Veneto-Trentina di Scienze Naturali residente in Padova
Palermo Accad. Atti	Atti della Reale Accademia di Scienze, Lettere e Belle Arti di Palermo
Palermo Circ. Mat. Rend	Rendiconti del Circolo Matematico di Palermo
Palermo, Effemeridi	Effermeridi scientifiche e letterarie per la Sicilia; coi Lavori del R. Instituto d'Incorraggiamento per la Sicilia
Palermo, Giorn. Sci Natur.	Giornale di Scienze naturali ed economiche, publicato per Cura della Societa di Scienze naturali ed economiche di Palermo
Palermo, Mem. Spettrosc Ital.	Memorie della Societa degli Spettroscopisti Italiani
Palermo Oss. Bull Meteorol.	Bullettino Meteorologico del Reale Osservatorio di Palermo
Palermo Oss Ossvz. Meteorol.	R. Osservatorio di Palermo. Stazioni di Valverde Osservazioni meteorologiche
Palomba, Raccolta	Raccolta di Lettere, etc , intonno alla Fisica ed alle Mathematiche
Palyamunkak	Palyamunkak. Termerzetlud (Prize Essays of the Hungarian Academy)
Pander, Beitr. Naturk.	Beitrage zur Naturkunde aus den Ostseeprovinzen Russlands
Paper	Paper
Paper-Maker Brit. Trade J.	Paper Maker and British Trade Journal
Paper Makers' Monthly J.	Paper Makers' Monthly Journal
Paper Making	Paper Making
Paper Mill	Paper Mill and Woodpulp News
Papers Naval Archit.	Papers on Naval Architecture and other subjects connected with naval science
Paper Trade J.	Paper Trade Journal
Papier-Fabr.	Papier-Fabrikant, Der
Papier Ztg.	Papier Zeitung
Papierhandel	Der Papierhandel
Papilio	Papilio
Papir J.	Papir Journalen
Par. P.	Paraguay Patent
Para, Mus. Hist. Natur Bol.	Boletim do Museu Paraense de Historia Natural e Ethnographia
Paris, Acad Med. Bull.	Bulletin de l'Academie de Medecine

Paris, Acad. Med. Mem.	Memoires de l'Academie de Medecine
Paris, Acad. Sci. Compt. rend.	Comptes Rendus hebdomadaires des Seances de l'Academie des Sciences
Paris, Acad. Sci. Mem.	Memoires de l'Academie des Sciences de l'Institut de France
Paris, Ann. Cerc. Med.	Annales du Cercle Medicale
Paris, Ann. Conserv.	Annales du Conservatoire des Arts et Metiers
Paris, Ann. Ecole Norm.	Annales scientifiques de l'Ecole Normale Superieure
Paris, Ann. Ponts Chauss.	Annales des Ponts et Chaussees. Memoires et documents relatifs a l'Art des Constructions et au Service de l'Ingenieur
Paris, Ann. Soc. Entom.	Annales de la Société Entomologique de France
Paris, Annaes Sci.	Annaes das Sciencias, etc, por huma Sociedade de Portuguezes residentes em Paris
Paris, Annu. Med. Chir. Hosp.	Annuaire medico chirurgical des Hopitaux, etc, de Paris
Paris, Annu. Soc. Met.	Annuaire de la Société Meteorologique de France
Paris, Anthropol. Soc Bull.	Bulletin de la Société d'Anthropologie de Paris
Paris, Anthropol Soc Mem.	Memoires de la Société d'Anthropologie de Paris
Paris, Bull Fac. Med.	Bulletins de la Faculte de Medecine de Paris et de la Société etablie dans son sein
Paris, Bull. Soc Aerost.	Bulletin de la Société Aerostatique et Meteorologique de France
Paris, Bull. Soc Sci. Natur.	Bulletin de la Société des Sciences Naturelles de France
Paris, Bur. Long. Annu	Annuaire pour l'An.. publie par le Bureau des Longitudes
Paris, Caus. Sci.	Causeries Scientifiques de la Société Zoologique de France
Paris, Club Alpin Franc Annu.	Annuaire du Club Alpin Francais
Paris, Com Intl Carte Ciel Bull	Institut de France. Academie des Sciences Bulletin du Comite International Permanent pour l'Execution Photographique de la Carte du Ciel
Paris Congr. Bot. Act.	Actes du Congres International de Botanique tenu a Paris in aout 1867
Paris Congr. Bot. Compt. rend.	. Comptes Rendus . Congres International de Botanique et d'Horticulture
Paris, Congr. Med Intl.	Congres Medical International de Paris, 1867
Paris, Ecole Norm Ann.	Annales Scientifiques de l'Ecole Normale Superieure, publies sous les auspices du Ministre de l'Instruction Publique
Paris, Ecole Poly. Corresp.	Correspondance sur l'Ecole Polytechnique, a l'usage des Eleves de cette Ecole
Paris, Ecole Poly. J.	Journal de l'Ecole Polytechnique publie par le Conseil d'Instruction de cet Etablissement
Paris, Ethnog. Soc. Compt rend.	Comptes Rendus des Seances de la Société d'Ethnographie Americaine et Orientale
Paris, Hautes Etudes Bibl.	Bibliotheque de l'Ecole des Hautes Etudes ..Section des Sciences Naturelles
Paris, Ingen. Civ. Mem.	Memoires et Compte Rendu des Travaux de la Société des Ingenieurs Civils (de France)
Paris, J. Bot.	Journal de Botanique, par une Société de Botanistes
Paris, J. Chir.	Journal de Chirurgie
Paris, Lab. Histol. Trav.	Ecole Pratique des Hautes Etudes. Laboratoire d'Histologie du College de France. Travaux
Paris, Mem. Acad. Med.	Memoires de l'Academie (Royale) de Medecine
Paris, Mem. Acad. Sci.	Memoires de l'Academie des Sciences
Paris, Mem. Inst.	Memoires de la Classe des Sciences mathematiques et physiques de l'Institut

Paris, Mem. Soc. Savants	Memoires des Sociétés Savants et Litteraires de la Republique Francaise
Paris, Mem Savants Etrang.	Memoires presentes par divers Savants a l'Academie des Sciences de l'Institut de France
Paris, Mem Soc Ethnol	Memoires de la Société Ethnologique
Paris, Mem Soc Fac. Med.	Memoires de la Société de la Faculte de Medecine
Paris, Mem. Soc. Linn	Memoires de la Société Linneenne de Paris
Paris, Mem Soc. Med	Memoires de la Société de Medecine
Paris, Mem. Soc. Med. Observ.	Memoires de la Société Medicale d'Observation
Paris, Mus. Hist. Natur. Ann.	Annales du Museum d'Histoire Naturelle
Paris, Mus Hist. Natur. Archiv.	Archives du Museum d'Histoire Naturelle
Paris, Mus Hist Natur. Bull.	Bulletin du Museum d'Histoire Naturelle
Paris, Mus. Hist Natur. Cent	Centenaire de la Fondation du Museum d'Histoire Naturelle
Paris, Mus Hist. Natur. Mem	Memoires du Museum d'Histoire Naturelle
Paris, Mus Hist Natur. Nouv Ann.	Nouvelles Annales du Museum d'Histoire Naturelle
Paris, Mus. Hist Natur Nouv. Archiv.	Nouvelles Archives du Museum d'Histoire Naturelle
Paris Obs. Ann.	Annales de l'Observatoire de Paris
Paris, Obs Montsouris Annu.	(Ville de Paris) Annuaire de l'Observatoire (municipal de Paris, dit Observatoire) de Montsouris ..
Paris, Poids Mes Proc-Verb	Comite International des Poids et Mesures. Proces-Verbaux des Seances
Paris, Poids Mes Trav. Mem	Travaux et Memoires du Bureau International des Poids et Mesures
Paris, Recueil Soc. Med. Observ	Recueil des travaux de la Société Medicale d'Observation de Paris
Paris, Recueil Trav. Soc Med Allemande	Recueil des Travaux lus a la Société Medicale Allemande de Paris
Paris, Soc Acclim Bull.	Bulletin de la Société Zoologique d'Acclimatation
Paris, Soc Anat Bull.	Bulletin de la Société Anatomique de Paris
Paris, Soc Anthrop Bull	Bulletins de la Société d'Anthropologie de Paris
Paris, Soc. Anthrop. Mem	Memoires de la Société d'Anthropologie de Paris
Paris, Soc Biol Mem	Comptes Rendus des Seances et Memoires de la Société de Biologie
Paris, Soc. Chir. Bull	Bulletin de la Société de Chirurgie de Paris
Paris, Soc. Chir Mem	Memoires de la Société de Chirurgie de Paris
Paris, Soc. Entom Ann	Annales de la Société Entomologique de France
Paris, Soc Entom Bull	Bulletin de la Société Entomologique de France
Paris, Soc. Geogr. Bull.	Bulletin de la Société de Geographie
Paris, Soc. Geogr Compt. rend.	Compte Rendu des Seances de la Société de Geographie et de la Commission Centrale
Paris, Soc Hist Natur Mem.	Memoires de la Sociéte d'Histoire Naturelle de Paris
Paris, Soc Ing. Civ. Mem.	Memoires et Comptes Rendus des Travaux de la Société des Ingenieurs Civils
Paris Soc. Linn. Bull.	Bulletin mensuel de la Société Linneenne de Paris
Paris, Soc Math. Bull.	Bulletin de la Société Mathematique de France
Paris, Soc. Med Emul Bull	Bulletins de la Société Medicale d'Émulation
Paris, Soc. Med. Emul. Mem.	Memoires de la Société Medicale d'Émulation
Paris, Soc. Philom. Bull	Bulletin des Sciences de la Société Philomathique de Paris

Paris, Soc. Philom Mem Cent.	Memoires publies par la Société Philomathique a l'occasion du Centenaire de sa Fondation, 1788-1888
Paris, Soc. Philom Nouv Bull	Nouveau Bulletin des Sciences de la Société Philomatique de Paris
Paris, Soc Philom Proc Verb.	Extraits des Proces-Verbaux des Seances de la Société Philomatique
Paris, Soc Phys Seances	Seances de la Société Francaise de Physique
Paris, Soc. Speleol. Mem	Memoires de la Société de Speleologie
Paris Tow. Nauk Scisl. Pam	Pamietnik Towarzystwa Nauk Scislych w Paryzu
Paris, Trav Soc. Amat	Notice des Travaux de la Société des Amatuers des Sciences physiques et naturelles de Paris
Parlatore, Giorn. Bot.	Giornale Botanico Italiano
Parma, Giorn Soc Med. Chir.	Giornale della Societa Medico Chirurgica di Parma
Passau Ber Nat Ver	Bericht des Naturhistorischen Vereins in Passau fur
Passau, Jahr Naturhist Ver	Jahresbericht des Naturhistorischen Vereins
Pathol Soc Trans	Transactions of the Pathological Society of London
Pavia Ist Bot Atti	Atti dell' Istituto Botanico dell' Universita di Pavia. Seguito dell' Archivio Triennale del Laboratorio di Botanica Crittogamica
Pavia Lab Crittog. Archiv.	Archivio del Laboratorio di Botanica Crittogamica presso la R Universita di Pavia
Peabody Acad Mem	Memoirs of the Peabody Academy of Science
Peabody Acad. Report	Sixth Annual Report of the Trustees of the Peabody Academy of Science
Penn Univ Publ.	Publications of the University of Pennsylvania
Penzance Soc Trans	Transactions of the Natural History and Antiquarian Society of Penzance
Perf Essent Oil Rec	Perfumery and Essential Oil Record
Perthsh Soc Sci Trans & Proc.	Transactions and Proceedings of the Perthshire Society of Natural Science
Peru P	Peruvian Patent
Pet Nouv Entom	Petites Nouvelles Entomologiques
Petermann, Mitth	Dr A Petermann's Mittheilungen aus Justus Perthes' Geographischer Anstalt
Peters, Zts	Zeitschrift fur populare Mittheilungen aus dem Gebiete der Medicin, Chirurgie, und Pharmacie; in Verbindung mit einem Vereine von Aerzten und Pharmaceuten der Herzogthumer Schleswig und Holstein
Petroleum	Petroleum
Petroleum Gaz	Petroleum Gazette
Petroleu m Rev.	Petroleum Review
Pfluger, Archiv Physiol	Archiv fur die gesammte Physiologie des Menschen und der Thiere
Pharm.	Pharmakologie
Pharm.-Ber Deut.-Arzbuch.	Pharmakopoe-Bericht Die vegetabilischen Drogen des Deutschen Arzneibuches, 5^te. Ausgabe, Caesar & Loretz, Halle
Pharm. Centr.	Pharmaceutisches Central-Blatt
Pharm Centralh.	Pharmaceutische Centralhalle fur Deutschland
Pharm. Era	Pharmaceutical Era
Pharm. J.	The Pharmaceutical Journal (and Transactions)
Pharm. Post	Pharmazeutische Post
Pharm. Weekblad	Pharmazeutische Weekblad
Pharm Ztg.	Pharmazeutische Zeitung

Pharm. Zts.	Pharmazeutische Zeitschrift
Pharm. Zts. Russland	Pharmaceutische Zeitschrift für Russland
Phil. Mag.	Philosophical Magazine
Phil Stud.	Philosophische Studien
Phil. Trans.	Philosophical Transactions of the Royal Society of London
Phila. Acad. Natur. Sci. J.	Journal of the Academy of Natural Sciences of Philadelphia
Phila., Acad. Natur. Sci. Proc.	Proceedings of the Academy of Natural Sciences of Philadelphia
Phila. Amer. Entom. Soc.	See Amer. Entom. Soc.
Phila. Coll. Pharm. Journ.	Journal of the Philadelphia College of Pharmacy
Phila. Eng. Club	Proceedings of the Engineers' Club of Philadelphia
Phila. Entom. News	Entomological News (and Proceedings of the Entomological Section of the Academy of Natural Sciences of Philadelphia)
Phila. Entom. Soc. Proc.	Proceedings of the Entomological Society of Philadelphia
Phila. Med. Mus.	Philadelphia Medical Museum
Phila. Med. Phys J.	The Philadelphia Medical and Physical Journal
Phila. Phot.	The Philadelphia Photographer
Philippine J. Sci.	Philippine Journal of Science
Phot. Archiv	Photographisches Archiv
Phot. Bull.	Anthony's Photographic Bulletin
Phot. Chronik.	Photographische Chronik und allgemeine Photographen-Zeitung
Phot. J.	Wilhelm Horn's Photographische Journal
Phot. Corr. (Korr)	Photographische Korrespondenz
Phot. Mag.	Photographisches Magazine
Phot. Mitth.	Photographische Mittheilungen
Phot. Monats.	Photographische Monatshefte
Phot. News	Photographic News
Phot. Rundsch.	Photographische Rundschau und Photographisches Centralblatt
Phot. Soc. J.	Journal of the Photographic Society of London
Phot. Soc. Trans.	Trans of the Photographic Society of London
Phot. Times	The Photographic Times
Phot. Wochenbl.	Photographisches Wochenblatt
Phot. World	The Photographic World
Phot. Centr.	Photographisches Centralblatt
Phot. Ztg.	Deutsche Photographen-Zeitung
Phys. Rev.	Physical Review
Physikal.-Chem. Zentr.	Physikalisch-chemisches Zentralblatt
Physikal Meddel.	Physikalske Meddelelser
Physikal. Zts.	Physikalische Zeitschrift
Physiol. Russe	Le Physiologiste Russe
Physiol. Soc. Proc.	See J. Physiol.
Phytologist	The Phytologist: a popular Botanical Miscellany
Pisa, Ann. Scuola Norm.	Annali della R. Scuola Normale Superiore di Pisa. Scienze Fisiche e Matematiche
Pisa, Ann. Univ. Tosc. Sci. Cosm.	Annali della Universita Toscana. Scienze Cosmologiche
Pisa, Miscell. Med. Chir.	Miscellanea medico-chirurgico-farmaceutiche raccolte in Pisa
Pisa, Nuov. Giorn.	Nuovo Giornale de' Letterati
Pisa Soc. Sci. Proc.	Atti della Société Toscana di Scienze Naturali residente in Pisa

Pisa Soc. Tosc. Atti (Mem.)	Atti della Societa Toscana di Scienze Naturali residente in Pisa. Memorie
Pisa Soc. Tosc Atti (Proc. Verb.)	Arti della Societa Toscana di Scienze Naturali residente in Pisa. Processi Verbali
Pistoja, Atti Accad.	Atti della R. Accademia Pistojese di Scienze, Lettere, ed Arti; Memorie di Matematica e Fisca
Plant World	Plant World, The
Plata Mus. Anales	Anales del Museo de La Plata. Materiales para la Historia fisica y moral del Continente Sud-Americano
Plata Mus Revista	Revista del Museo de La Plata
Plön Biol. Sta. Forschungsber.	Forschungsberichte aus der Biologischen Station zu Plon
Plymouth Inst. Trans	Annual Reports and Transactions of the Plymouth Institution and Devon and Cornwall Natural History Society
Pogg. Ann.	Poggendorff's Annalen der Physik und Chemie
Pogg. Ann. Beibl.	Poggendorff's Annalen der Physik und Chemie Beiblatter
Poligrafo	Il Poligrafo. Giornale di Science, Lettere, ed Arti
Polit.	Il Politecnico
Pollichia, Jahr.	Jahresbericht der Pollichia, eines naturwissenschaftlichen Vereins der Baierischen Pfalz (der Rheinpfalz)
Polsk. Tow Przyrod Kopernika	See Kosmos (Lwow)
Poly. Centr	Polytechnisches Centralblatt
Poly. Centralh.	Polytechnische Centralhalle
Poly Mitth.	Polytechnische Mittheilungen
Poly. Notiz.	Polytechnisches Notizblatt
Polygraph Centr.	Polygraphisches Centralblatt
Pommer, Zts	Schweizerische Zeitschrift fur Natur- und Heilkunde
Pop Mag. Anthropol.	The Popular Magazine of Anthropology
Pop Sci Mon.	Popular Science Monthly
Popular Sci Rev.	The Popular Science Review a Quarterly Miscellany of entertaining and instructive articles on Scientific subjects
Pontif Univ. Gregor	Pontificia Universita Gregoriana. Continuazione del Bullettino Meteorologico dell' Observatorio del Collegio Romano
Port. P.	Portuguese Patent
Portland, Soc. Natur Hist. Proc.	Proceedings of the Portland Society of Natural History
Porto, Ann. Soc Lit.	Annaes da Sociedade Lit Portuense
Porto Soc. Instruc. Rev.	Revista da Sociedade de Instruccao do Porto
Potsdam Astrophys Obs. Publ.	Publicationen des Astrophysikalischen Observatoriums zu Potsdam
Pottery Gaz.	Pottery Gazette
Pottery and Glass	Pottery and Glass
Power	Power
Prace Mat.-Fiz.	Prace Matematyczno-Fizyczne. (Mathematical and Physical Papers)
Pract. Drug.	Practical Druggist and Pharmaceutical Review of Reviews, New York
Pract. Mag.	The Practical Magazine (London)
Pract. Mechan. J.	The Practical Mechanics Journal
Practitioner	The Practitioner
Prag, Abh.	Pojednani Kral. Ceske Spolecnosti Nauk. Abhandlungen der Königl. Böhmischen Gesellschaft der Wissenschaften

Prag, Ceske Ak Fr Jos. Pam	Pomatnik na oslavu padesaitketeho panovnickeho Jubilea jeho Velicenstva Cisare a Krale Frantiska Josefa I. Vydala Ceska Akademie Cisare Frantisks Josefa pro Vedy, Slovesnost a Umeni. (Memoira in celebration of the fifty years Jubilee of the reign of H I & R M. Francis Joseph I. Published by the Bohemian Imperial Francis Joseph Academy of Science, Literature and Art)
Prag, Ceske Akad. Fr Jos Rozpr. (Trida 2)	Rozpravy Ceske Akademie Cisare Frantiska Josefa pro Vedy, Slovesnost a Umeni v Praze. (Trida II.) (Transactions of the Bohemian Imperial Francis Joseph Academy of Science, Literature and Art in Prague. Class II)
Prag Fr Jos Acad Sci Bull.	Academie des Sciences de l'Empereur Francois Joseph I Bulletin International
Prag, Jahr. Bohm Mus	Jahrbucher des Bohmischen Museums fur Natur- und Landerkunde
Prag, Jahr Realschule	Jahresbericht der k. k. Bohmischen Ober-Realschule zu Prag
Prag, Lotos Abh	Abhandlungen des Deutschen Naturwissenschaftlich-Medicinischen Vereines fur Bohmen "Lotos"
Prag, Monatschr Mus	Monatsschrift der Gesellschaft des vaterlandischen Museums in Bohmen
Prag, Sitzber	Zpravy o Zasedani (Vestnik) Kralovske Ceske Spolecnosti Nauk. Trida. Mathematicko-Prirodovedecka. Sitzungsberichte der Konigl Bohmischen Gesellschaft der Wissenschaften. Mathematisch-Naturwissenschaftliche Classe
Prag Sternw Magn Meteorol. Beob	Magnetische und Meteorologische Beobachtungen an der K K Sternwarte zu Prag
Prag, Verh.	Verhandlungen der Gesellschaft des vaterlandisches Museums in Bohmen
Prag, Vierteljahrschr	Vierteljahrschrift fur die praktische Heilkunde
Pressburg, Corresp Blatt	Correspondenzblatt des Vereins fur Naturkunde zu Pressburg
Pressburg, Verh.	Verhandlungen des Vereins fur Naturkunde zu Pressburg
Presse Sci	Presse Scientifique des Deux Mondes
Preuss Bot Ver Sitzber	See Konigsberg Schriften
Preuss. Geod Inst. Publ	Publication des Konigl Preuss. Geodatischen Instituts
Preuss. Geod Inst Veroff	Veroffentlichung des Konigl Preussischen Geodatischen Instituts
Preuss Landes-Oekon -Kolleg Archiv	See Landw. Jbuch
Pribram Bergakad	See Wien, Berg- u Huttenm. Jbuch
Princeton Mus Contr.	Contributions from the (E. M.) Museum of Geology and Archaeology of Princeton College
Pringsheim, Jahr Wiss Bot.	Jahrbucher fur Wissenschaftliche Botanik
Print Reg	Printers' Register
Prog. agric Viti	Progres agricole et viticole
Proc Amer Acad	Proceedings of the American Academy of Arts Sciences
Proc. Amer. Inst Elec. Eng	Proceedings of the American Institute of Electrical Engineers
Proc. Amer Micro Soc.	Proceedings of the American Microscopical Society
Proc Amer. Pharm. Assoc.	Proceedings of the American Pharmaceutical Association
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society

Proc Amer. Soc. Civil Eng.	Proceedings of the American Society of Civil Engineers
Proc. Amer. Soc Micro	Proceedings of the American Society of Microscopists
Proc Amer. Soc. Test. Mat.	Proceedings of the American Society for Testing Materials
Proc Amer Water Works Assoc.	Proceedings of American Water Works Association
Proc Assoc Off Agric Chem	Proceedings of the Association of Official Agricultural Chemists, Washington
Proc Austral Inst. Min Eng	Proceedings Australian Institute of Mining Engineers
Proc Cambr Phil Soc	Proceedings of the Cambridge Philosophical Society
Proc Chem Soc	Proceedings of the Chemical Society (London)
Proc. Eng Soc Western Penn	Proceedings of the Engineers' Society of Western Pennsylvania
Proc. Inst Civil Eng	Proceedings of the Institution of Civil Engineers
Proc Inst Mech Eng.	Proceedings of the Institution of Mechanical Engineers
Proc Natl Wholesale Drug Assoc	Proceedings of the National Wholesale Druggists' Association
Proc Physiol Soc	Proceedings of the Physiological Society
Proc Roy Soc. Edinb	Proceedings of the Royal Society of Edinburgh
Proc. Roy. Soc London	Proceedings of the Royal Society of London
Proc Roy. Soc Med	Proceedings of the Royal Society of Medicine
Proc Soc Exp Biol Med	Proceedings of the Society for Experimental Biology and Medicine
Proc U S Naval Inst	Proceedings of U S Naval Institute
Progres Med	Le Progres Medical Journal de Medecine, de Chirurgie et de Pharmacie
Progressive Age	Progressive Age
Propogation ind	La Propogation industrielle Revue mensuelle illustre des inventions, machines, appareils et procedes de la France, etc
Prov Med Assoc J	Journal of the Provincial Medical Association
Prov Med Surg Assoc Trans	Transactions of the Provincial Medical and Surgical Association
Psyche	Psyche Organ of the Cambridge Entomological Club
Psychol Med J	Journal of Psychological Medicine
Publ Carnegie Inst	Publications of the Carnegie Institution of Washington
Publ ind.	Publication industrielle des machines par Armengaud
Public Analysts Proc	Proceedings of the Society of Public Analysts
Public Health	Public Health
Pulp Paper Mag. Can	Pulp and Paper Magazine of Canada
Pure Products	Pure Products Scientific Station for Pure Products, New York
Puy, Soc Agric Ann	Annales de la Société d'Agriculture, Sciences, etc , du Puy
Quart. J. Chem Soc.	Quarterly Journal of the Chemical Society
Quart. J. Dent. Sci	Quarterly Journal of Dental Science
Quart. J. exp. Physiol	Quarterly Journal of experimental Physiology
Quart. J. Geol Soc	Quarterly Journal of the Geological Society
Quart J. Math.	The Quarterly Journal of Pure and Applied Mathematics
Quart J. Micro. Sci	Quarterly Journal of Microscopical Science
Quart. J. Micro Soc	Quarterly Journal of the Microscopical Society
Quart J Sci.	The Journal of Science and the Arts Continued as the Quarterly Journal of Science, Literature, and Arts

Quebec, Lit. Hist. Soc. Trans.	Transactions of the Literary and Historical Society of Quebec
Queensl P.	Queensland Patent
Queensl. Annu. Rep. Brit. N. Guinea	Annual Report on British New Guinea
Queensl. Natur. Hist Soc. Trans.	Transactions of the Natural History Society of Queensland
Queensl Mus Ann	Annals of the Queensland Museum
Queensl. Roy. Soc. Proc.	The Proceedings of the Royal Society of Queensland
Quekett Micro. Club J.	Journal of the Quekett Microscopical Club
Quetelet, Corresp. Math.	Correspondance Mathematique et Physique
Radium	Radium, Le
Railroad Eng. J	The Railroad and Engineering Journal. The American Railroad Journal and Van Nostrand's Engineering Magazine have been consolidated in this publication
Ranuzzi, Annuario Geogr.	Annuario geographico Italiano
Rass. minerar.	Rassegna mineraria metallurgica e chimica
Rauch Staub	Rauch und Staub
Rayer, Archiv.	Archives de Medecine comparee
Reclam, Kosmos	Kosmos Zeitschrift fur angewandte Naturwissenschaften
Records Min.	Records of Mining
Recueil Math. (Moscou)	Recueil Mathematique. Publie par la Société Mathematique de Moscou
Rec. Trav. Chim. Pays-Bas	Recueil des Travaux Chimiques des Pays-Bas (et de la Belgique)
Rec. Zool Suisse	Recueil Zoologique Suisse, comprenant l'Embryologie, l'Anatomie et l'Histologie comparees, la Physiologie, l'Ethologie, la Classification des Animaux vivants et fossiles
Regensburg Bot. Ges	See Flora
Regensburg Bot. Ges. Denkschr	Denkschriften der Koniglich (Bayerischen) Botanischen Gesellschaft zu Regensburg
Regensburg, Bot. Ztg.	Botanische Zeitung, herausg von der k. Baier. Botanischen Gesellschaft zu Regensburg
Regensburg, Korresp Blatt.	Korrespondenz-Blatt des Zoologischmineralogischen Vereins in Regensburg
Reichert, Archiv	Archiv fur Anatomie, Physiologie, und wissenschaftliche Medicin
Reil, Archiv	Archiv fur die Physiologie
Reimann's Ztg.	Reimann's Färberzeitung
Reims, Seances Acad.	Seances et Travaux de l'Academie de Reims
Rend. soc. chim. ital.	Rendiconti della societa chimica italiana
Rep.	Repertorium, Repertoire Repertory
Rep Anal Chem.	Repertorium der analytischen Chemie . .Organ des Vereins Analytischer Chemiker
Rep. Anat. Physiol.	Repertoire generale d'Anatomie et de Physiologie pathologiques et de Clinique chirurgicale
Rep. Chim.	Repertoire generale de Chimie (1901–), G. Jaubert
Rep. Chim. pure (appl)	Repertoire de Chimie pure (et appliquée) (Societe Chimique de Paris, 1859–1864)
Rep. Pat. Inv	The Repertory of Patent Inventions and other discoveries and improvements in arts, manufactures and agriculture
Rep. Math.	Repertorium der literarischen Arbeiten aus dem Gebiete der reinen und angewandten Mathematik

Rep. Meteorol.	Repertorium fur Meteorologie, herausgegeben von der Kaiserlichen Akademie der Wissenschaften
Rep. Pharm.	Repertorium fur die Pharmacie
Rep. Phys.	Repertorium der Physik
Rep. Phys.-Tech.	See Carl
Rep. Chem. Lab. Amer. Med. Ass.	Reports of the Chemical Laboratory of the American Medical Association, Chicago
Rep. Council Pharm. Chem.	Reports of the Council of Pharmacy and Chemistry, American Medical Association, Chicago
Rep. H. M. Insp. Expl.	Report of His Majesty's Inspectors of Explosives
Rep. N. Y. Bd. Pharm.	Report of the New York State Board of Pharmacy
Rev. Anthrop.	Revue d'Anthropologie
Rev. Artill.	Revue d'Artillerie
Rev. Biol. Nord France	Revue Biologique du Nord de la France
Rev. Bot.	Rev. de Botanique. Bulletin mensuel de la Société Francaise de Botanique
Rev. Bryol.	Revue Bryologique. Bulletin bimestriel consacre a l'Etude des Mousses et des Hepatiques
Rev. chim. ind.	Revue de chimie industrielle et La revue de physique et de chimie
Rev. Cours. Sci.	Revue des Cours Scientifiques de la France et de l'Etranger
Rev. deux Mondes	Revue des deux Mondes (Paris)
Rev. Entom.	Revue d'Entomologie publiee par la Société Francaise d'Entomologie
Rev. gen. Bot.	Revue generale de Botanique
Rev. gen. chim	Revue generale de chimie pure et appliquee (G. Jaubert)
Rev. gen. lait	Revue generale du lait
Rev. gen. mat. color.	Revue generale de matieres colorantes et de leurs applications aux textiles
Rev. gen. sci.	Revue generale des sciences pure et appliquee
Rev. Hortic.	Revue Horticole, Journal d'Horticulture pratique
Rev. hyg. pol. sanitaire	Revue d'hygiene et de police sanitaire
Rev. Ind.	Revue Industrielle
Rev. Ind. Chim.	Revue des industries chimiques et agricoles
Rev. Mag. Zool.	Revue et Magazin de Zoologie, pure et appliquee
Rev. Maritime Colon	Revue Maritime (et Coloniale)
Rev. Med. Chir.	Revue Medico Chirurgicale de Paris
Rev. Med. Franc. Etrang.	Revue Medicale Francaise et Etrangere
Rev. Met.	Revue de Metallurgie
Rev. Mycol.	Revue Mycologique. Recueil trimestriel illustre consacre a l'Etude des Champignons
Rev. phot.	Revue de photographie
Rev. Quest. Sci.	Revue des Questions scientifiques publiee par la Société Scientifique de Bruxelles
Rev. Sci.	(la) Revue Scientifique (de la France et de l'Etranger Revue des Cours Scientifiques)
Rev. Sci. Natur.	Revue des Sciences Naturelles
Rev. Soc. Hyg. Aliment.	Revue de la société scientifique d'Hygiene alimentaire et de l'alimentation rationelle de l'homme
Rev. Suisse Zool.	Revue Suisse de Zoologie (et) Annales (de la Société Zoologique Suisse et) du Musee d'Histoire Naturelle de Geneve
Rev. Univ. Mines	Revue universelle des Mines, de la Metallurgie, des Travaux Publics, des Sciences et des Arts Appliquee a l'Industrie. Annuaire de l'Association des Ingenieurs sortis de l'Ecole de Liege

Rev. Vit	Revue Viticulture
Rev Zool.	Revue Zoologique, par la Société Cuvierienne
Revista Brazil	Revista Brazileira, Journal de Sciencias, Lettras, e Artes
Revista, Chim pure app	Revista de chimica pure applicada
Revista ind agric Tucuman	Revista industrial y agrocola de Tucuman
Revista Ligure	Revista Ligure, giornale di Lettere, Scienze, etc.
Revista Med Chile	Revista medica de Chile
Revista Med Cirug Habana	Revista de Medicina y Cirugia, Habana
Revista Minera	Revista Minera, periodico cientifico e industrial
Revista real acad. cien Madrid	Revista de la real academia de ciencias de Madrid
Revista Telegr	Revista de Telegrafos
Revista Trim Microgr	Revista Trimestral Micrografica. Organo del Laboratorio Histologico de la Facultad de Medicina de Madrid
Rhea	Rhea, Zeitschrift fur die gesammte Ornithologie
Rheinische Monatsschr	Rheinische Monatsschrift fur praktische Aerzte
Rheinl. Westphal	See Bonn.
Rheinl Westphal Corresp	Correspondenzblatt des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens
Rheinl Westphal Verh	Verhandlungen des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens
Rheinl. Westphal Sitzber	Sitzungsbericht des Naturhistorischen Vereins der Preussischen Rheinlande und Westphalens
Rheinpfalz Pollichia Festschr.	Festschrift zur Funfzigjahrigen Stiftungsfeier der Pollichia, Naturwissenschaftlichen Vereines der Rheinpfalz
Rheinpfalz Pollichia Jahr.	Jahresbericht der Pollichia, eines Naturwissenschaftlichen Vereins der Rheinpfalz
Rheinpfalz Pollichia Mitth	Mittheilungen der Pollichia, eines Naturwissenschaftlichen Vereins der Rheinpfalz
Rheinpfalz Pollichia Sep-Ausg	...Separat-Ausgabe der Pollichia, des Naturwissenschaftlichen Vereines der Pfalz
Rhodora	Rhodora. Journal of the New England Botanical Club
Riga, Arb. Naturf Ver.	Arbeiten des Naturforschenden Vereins in Riga
Riga, Corresp. Blatt. Naturf. Ver.	Correspondenz-Blatt des Naturforschenden Vereins in Riga
Rio de Janeiro Archiv Palestr.	Archivos da Palestra Scientifica do Rio de Janeiro
Rio de Janeiro Mus Nac. Archiv	Archivos do Museu Nacional do Rio de Janeiro
Rio de Janeiro Mus. Nac Revista	Revista do Museu Nacional do Rio de Janeiro.. (Seguimento aos Archivos do Museu Nacional)
Rio de Janeiro Obs Annaes	(Annaes do Imperial Observatorio do Rio de Janeiro)
Rio de Janeiro Obs. Bol.	Boletim mensal do Observatorio do Rio de Janeiro
Rio de Janeiro Obs Revista.	Revista do Observatorio. Publicacao mensal do Imperial Observatorio do Rio de Janeiro
Rio, Revista	Revista tri mensal de Historia e Geographis: Journal do Instituto Historico e Geographico Brasileiro
Rio, Soc Vell Trabal	Trabalhos da Sociedade Vellosiana (Bibliotheca Guanabarense)
Riv.	Rivista
Riv. Bolognese	Rivista Bolognese di Scienze e Lettere
Riv Geogr Ital.	Rivista Geografica Italiana (e Bolletino della Societa di Studi Geografici e Coloniali in Firenze)

Riv. Ital. Sci. Natur Napoli	Rivista Italiana di Scienze Naturali e loro Applicazioni pubblicata per cura degli Aspiranti Naturalisti
Riv Ital Sci Natur Siena	Rivista Italiana di Scienze Naturali e Bollettino del Naturalista Collettore, Allevatore, Coltivatore
Riv. Mat.	Rivista di Matematica
Riv. Mineral Crist	Rivista di Mineralogia e Cristallografia Italiana
Riv. Patol. Veg	Rivista di Patologia Vegetale
Riv. Sci -Ind.	Rivista Scientifico-Industriale delle principali Scoperte ed Invenzioni fatte nelle Scienze e nelle Industrie
Riv. Sper di Freniatria	Rivista Sperimentale di Freniatria e di Medicina legale
Riv. Vit. Ital	Rivista di Viticoltura ed Enologia Italiana
Robin, J Anat	Journal de l'Anatomie et de la Physiologie normales et pathologiques de l'homme et des animaux
Rochelle	See under Charente Inf
Rochester Acad. Sci Proc	Proceedings of the Rochester New York Academy of Science
Rochester Trans. Elec. Med Assoc.	Transactions of the National Electic Medical Association at its Third Meeting, at Rochester, U. S.
Rock Products	Rock Products
Rohr, Notizen	Notizen aus dem Gebiete der practischen Pharmacie
Rollett	See Graz
Roma	See Congr. Med Int Atti, 1894
Roma, Atti Nuovi Lincei	Atti dell' Accademia Pontificia de' Nuovi Lincei
Roma, Atti Reale Accad	Atti della Reale Accademia dei Lincei
Roma, Corrisp Sci.	Corrispondenza Scientifica in Roma per le avanzamento delle Scienze, etc
Roma Ist Bot Annuario	Annuario del R. Istituto Botanico di Roma
Roma Lab Anat Norm Ric.	Ricerche fatte nel Laboratorio di Anatomia Normale della R Universita di Roma
Roma, Nuovi Lincei Mem	Memorie della Pontificia Accademia dei Nouvi Lincei
Roma, Oss Coll Rom Mem.	Memorie del R Osservatorio del Collegio Romano
Roma, R Accad Lincei	Atti della R Accademia dei Lincei
(Roma), Soc Ital. Mem	Memorie di Mathematica e di Fisica della Societa Italiana delle Scienze
Roma, Soc. Studi Zool Boll	Bolletino della Societa Romana per gli Studi Zoologici
Roma, Specola Vaticana Publ.	Pubblicazioni della Specola Vaticana
Roma, Uff. Centr Meterol Ann.	Annali dell' Ufficio Centrale di Meterologia Italiana
Romer, Archiv Bot	Archiv fur die Botanik
Roser Wunderlich, Archiv	Archiv fur physiologische Heilkunde Continued as the Archiv d. Heilk
Rotterdam Nieuwe Verh.	Nieuwe Verhandelingen van het Bataafsch Genootschap der Proefondervindelijke Wijsbegeerte Rotterdam
Rouen, Bull. Soc Emul	Bulletins (des travaux) de la Société Libre d'Émulation de Rouen
Rouen, Soc. Sci Bull.	Bulletin de la Société des Amis des Sciences Naturelles de Rouen
Rouen, Trav. Acad.	Precis analytique des Travaux de l' Academie des Sciences, Belles-Lettres, et Arts de Rouen
Roumanie Inst. Meteorol Ann.	Annales de l'Institut Meteorologique de Roumanie Annalele Institutului Meteorologio al Romaniei
Roy. Engin. Papers	Papers on subjects connected with the duties of the Corps of Royal Engineers
Roy. Inst. J.	Journal of the Royal Institution of Great Britain

Roy. Inst. Proc.	Notices of the Proceedings at the Meetings of the Members of the Royal Institution of Great Britain, with Abstracts of the Discourses delivered at the Evening Meetings
Roy. School Naval Archit. Ann.	The annual of the Royal School of Naval Architecture and Marine Engineering
Roy. Soc. Proc.	Abstracts of the Papers printed in the Philosophical Transactions of the Royal Society of London, from 1800 to 1854 inclusive. Continued as the Proceedings of the Royal Society of London
Rugby, Natur. Hist. Soc. Reports	Reports of the Rugby School Natural History Society
Russ. Annu. Geol. Mineral.	Russian Annual of Geology and Mineralogy
Russ. Annuaire Mines	Annuaire du Journal des Mines de Russie
Russ. Chem. Soc. J.	Journal of the Russian Chemical Society
Russ. Geogr. Ges. Denkschr.	Denkschriften der Russischen Geographischen Gesellschaft zu St. Petersburg
Russ. J. exp. Landw.	Russiches Journal fur experimentelle Landwirtschaft
Russ. Jahr. Pharm.	Russisches Jahrbuch der Pharmacie
Russ. P.	Russian Patent
Russ. Pharm. Zts.	Pharmaceutische Zeitschrift für Russland
Russ. Phys.-Chem. Soc. J.	Journal of the Russian Physico-Chemical Society of the Imperial University of St. Petersburg
Rust, Mag.	Magazin fur die gesammte Heilkunde, etc.
S. Africa Chem Metall. Soc.	The Journal of the Chemical and Metallurgical Society of South Africa
S. Africa Chem. Metall. Soc. Proc.	The Proceedings of the Chemical and Metallurgical Society of South Africa
S. Africa. Mus. Ann.	Annals of the South African Museum
S. Africa. Phil. Soc. Trans.	The Transactions of the South African Philosophical Society
S. Austral. P.	South Australian Patent
S. Austral. Roy. Soc. Mem.	Memoirs of the Royal Society of South Australia
S. Austral. Roy. Soc. Trans.	Transactions and Proceedings and Report of the Royal Society of South Australia
S. C. Med. Assoc. Trans.	Transactions of the South Carolina Medical Association
S. London Entom. Natur. Hist. Soc. Proc.	(Abstract of) Proceedings of the South London Entomological and Natural History Society
S. Wales Inst. Civ. Engin. Proc	Proceedings of the South Wales Institute of Civil Engineers
S. Wales Roy. Inst. Report	The annual report of the Council of the Royal Institution of South Wales, with Appendix of Original Papers on Scientific Subjects
Sächs. Ingen. Ver. Mitth.	Mittheilungen des Sächsischen Ingenieur-Vereins; herausg. v. d. Verwaltungsrathe des Vereins
Sachs. Meteorol. Inst. Abh.	Abhandlungen des Konigl. Sächs. Meteorologischen Institutes
Sächs. Thüring. Naturwiss. Ver.	See Zts. Naturwiss.
Salem	See Essex Institute
San Fernando Obs. Marina An.	Anales del Instituto y Observatorio de Marina de San Fernando
Sanitary Record	Sanitary Record and Journal of Municipal Engineering, The
Santiago Chile, Univ. Anales	(Republica de Chile.) Anales de la Universidad
Sao Paulo, Rev. Mus. Paulista	Revista do Museu Paulista

Riv. Ital. Sci. Natur Napoli	Rivista Italiana di Scienze Naturali e loro Applicazioni pubblicata per cura degli Aspiranti Naturalisti
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Roma, Oss Coll Rom Mem.	Memorie del R Osservatorio del Collegio Romano
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Roma, Specola Vaticana Publ.	Pubblicazioni della Specola Vaticana
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Rouen, Soc. Sci Bull.	Bulletin de la Société des Amis des Sciences Naturelles de Rouen
Rouen, Trav. Acad.	Precis analytique des Travaux de l' Academie des Sciences, Belles-Lettres, et Arts de Rouen
Roumanie Inst. Meteorol Ann.	Annales de l'Institut Meteorologique de Roumanie Analele Institutului Meteorologio al Romaniei
Roy. Engin. Papers	Papers on subjects connected with the duties of the Corps of Royal Engineers
Roy. Inst. J.	Journal of the Royal Institution of Great Britain

Sci. Amer. Suppl.	Scientific American Supplement
Sci. Can.	Scientific Canadian
Sci. Ind. Bull. Roure-Bertrand Fils	Scientific et Industrial Bulletin Roure-Bertrand Fils
Sci. Proc. Roy. Dublin Soc.	Scientific Proceedings of the Royal Dublin Society
Sci. Rev.	The Scientific Review and Journal of the Inventors Institute
Sci. Trans. Roy. Dublin Soc.	Scientific Transactions of the Royal Dublin Society
Scienz. Ital. Congr.	Nuovo Congresso degli Scienziati Italiani in Venezia; porzione geologica
Sclater, Ibis	The Ibis, a Magazine of General Ornithology
Scott. Arbor. Soc. Trans.	Transactions of the Scottish Arboricultural Society
Scott. Geogr. Mag.	The Scottish Geographical Magazine
Scott. Meteorol. Soc. J.	Journal of the Scottish Meteorological Society
Scott. Micro Soc. Proc. & Trans.	Proceedings and Transactions of the Scottish Microscopical Society
Scott. Natur.	A Magazine of Scottish Natural History (and Journal of the Perthshire Society of Natural Science)
Scott. Soc. Arts Trans.	Transactions of the Royal Scottish Society of Arts
Seeman, J. Bot.	The Journal of Botany, British and Foreign
Seifenfabr.	Seifenfabrikant, Der
Seifens. Ztg.	Seifensieder Zeitung und Revue uber die Harz, Fett und Oelindustrie
Seine (Dep. de la)	See (France) Soc Agr. Mem
Seine, Mem. Soc. Agric.	Memoires d'Agriculture par la Société Agricole de la Seine
Seine-et-Oise, Mem.	Memoires de la Société des Sciences Naturelles de Seine et Oise
Seism. J. Japan	Seismological Journal of Japan
Selenka, Archiv Zool.	Nederlandisches Archiv fur Zoologie
Semi-Ann. Rep. Schimmel & Co.	Semi-Annual Report, Schimmel & Co , Miltitz
Senckenberg. Naturf. Ges. Abh	Abhandlungen herausg. von der Senckenbergischen Naturforschenden Gesellschaft
Senckenberg, Naturf. Ges. Ber.	Bericht uber die Senckenbergische naturforschende Gesellschaft in Frankfurt am Main
Shanghai, J.	Journal of the North-China Branch of the Royal Asiatic Society
Shanghai, J. Lit Soc.	Journal of the Literary and Scientific Society of Shanghai
Shoe Lea. Reporter	Shoe and Leather Reporter
Shropsh. Soc. Trans.	Transactions of the Shropshire Archaeological and Natural History Society
Sicilia, Atti Soc. Acclim.	Atti della Societa di Acclimazione e di Agricoltura in Sicilia
Sidereal Messenger	The Sidereal Messenger
Siebenb. Karpath. - Ver. Jahr.	Jahrbuch des Siebenburgischen Karpathen-Vereins
Siebold, J. Geburtshülfe	Journal für die Geburtshülfe, Frauenzimmer, etc., von Elias von Siebold
Siebold Kölliker, Zts.	Zeitschrift für wissenschaftliche Zoologie
Siebold, Lucina	Lucina; eine Zeitschrift zur Vervollkommung der Entbindungskunst
Siena, Atti Accad.	Atti dell' Accademia delle Scienze di Siena detta de' Fisio-critici
Silbermann, Rev. Entom.	Revue Entomologique

Silliman, J.	The American Journal of Science and Arts
Singapore Roy. Asiat. Soc. J.	Journal of the Straits Branch of the Royal Asiatic Society. Singapore.
Sitzber. kais. Akad. Wiss. Wien.	Sitzungsberichte der kaiserlichen Akademie der Wissenschaften, Wien (Mathematisch-naturwissenschaftliche Klass) Abteilungen I, IIa, IIb, III
Sitzb könig Akad. Munchen	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften zu München
Sitzber. konig. Akad. Wiss. Berlin	Sitzungsber der koniglich preussischen Akademie der Wissenschaften zu Berlin
Sitzber. konig. preuss Akad.	Sitzungsberichte der koniglich preussischen Akademie der Wissenschaften
Skand. Archiv Physiol.	Skandinavisches Archiv für Physiologie
Skand. Naturf Forh.	Forhandlingar vid det af Skandinaviska Naturforskare och Lakare hallna Mote i Gotheborg
Skand. Naturf Mod. Forh	Forhandlingerne ved de Skandinaviske Naturforskeres 11te Mode i Kjobenhavn fra den 3die til den 9de Juli, 1873
Skand. Natur Möt Forh	Forhandlingar vid de Skandinaviska Naturforskarnes Tolfte Mote i Stockholm fran den 7 till den 14 Juli, 1880
Skandia	Skandia Tidskrift for Vetenskap och Konst; utgifven af Svenska Litteratur-Foreningen
Skofitz	See Oesterreich. Botan Zeitschr.
Skofitz, Bot. Wochenbl.	Oesterreichisches Botanisches Wochenblatt
Skofits, Bot. Zts	Oesterreichische Botanische Zeitschrift
Smithsonian Contrib	Smithsonian Contributions to Knowledge
Smithsonian Inst Astrophys Obs Ann	Annals of the Astrophysical Observatory of the Smithsonian Institution
Smithsonian Inst Bur. Ethnol Report	Annual Report of the Bureau of (American) Ethnology to the Secretary of the Smithsonian Institution
Smithsonian Misc Coll.	Smithsonian Miscellaneous Collections
Smithsonian Report	Annual Report of the Board of Regents of the Smithsonian Institution, showing the Operations, Expenditures and Condition of the Institution
Snelling's Phot. J.	Snelling's Photographisches Journal
Soc. Bot. Ital Bull.	See Nuovo Giorn. Bot. Ital.
Soc. Broteriana	See Coimbra, Soc. Broter. Biol.
Soc. Elvet. Sci. Naturf. Atti	See Schweiz. Naturf. Ges. Verh.
Soc Entom Ross Horae	Horae Societatis Entomologicae Rossicae variis sermonibus in Rossia usitatis editae
Soc. Franc. Bot.	See Rev. Bot.
Soc. Franc. Entom.	See Rev. Ent.
Soc. Freniatr. Ital.	See Riv. Sper. di Freniatria
Soc. Geogr. Finland	See Fennia
Soc. Helvet. Actes.	Actes de la Société Helvetique des Sciences Naturelles
Soc. Helvet. Sci. Naturf Act	See Schweiz. Natf. Ges. Verh
Soc. Ital. Antrop.	See Arch. Antropologia
Soc. Ital. Fis.	See Nuovo Cimento
Soc. Ital. Micro. Boll.	See Acireale, Soc. Ital. Micr. Boll.
Soc. Ital. Sci.	See (Roma), Soc. Ital. Mem.
Soc. Ital. Sci. Nat.	See Milano, Soc. Ital.
Soc. Ligust. Sci. Natur. Geogr.	See Genova, Soc. Ligust. Atti
Soc. Malacol. France	See Ann. Malacol.

Soc. Malacol. Ital. Bull.	See Bull. Malacol. Ital.
Soc. Meteorol. Ital.	See Moncalieri Oss. Boll.
Soc. Mex. Hist. Natur.	See Naturaleza
Soc. Napoli	Societa reale di Napoli. Rendiconto dell' Academia delle Scienze fisiche e mathematiche
Soc. Nat. Sicil.	See Nat. Sicil.
Soc. Pharm. Anvers	See J. de Pharm.
Soc. Public Analysts	See Analyst
Soc. Speleol.	See Spelunca, Paris
Soc. Telegr.-Engin. Elect.	See Telegr. Eng. J.
Soc. Tosc. Sci. Nat.	See Pisa Soc. Tosc.
Soc. Ven.-Trent. Sci. Nat.	See Padova Soc. Sci.
Soc. Zool. Suisse Ann.	See Rev. Suisse Zool.
Soc. Zool. Tokyo	See Annot. Zool. Jap.
Somerset. Archaeol. Soc. Proc.	Proceedings of the Somersetshire Archaeological and Natural History Society
Somerset. Sov. Proc.	Somersetshire Archaeological and Natural History Society's Proceedings
Somme (Dep. de la)	See under Amiens
Southern Pharm. J.	Southern Pharmaceutical Journal
Span. P.	Spanish Patent
Spatula	Saptula (The), Boston
Spelunca Paris	Spelunca. Bulletin de la Société de Speleologie
Sperimentale	Lo Sperimentale. Giornale Italiano di Scienze Meidche
Spettatore Vesuvio	Lo Spettatore del Vesuvio e de' Campi Flegrei
Spettrosc. Ital. Mem.	Memorie della Societa degli Spettroscopisti Italiani
Spongia, Comm Med.	Commentarii di Medicina
Sprechsaal	Sprechsaal
Spregnel, Jahr.	Jahrbücher der Gewächskunde
Sprengst Waffen Mun.	Sprengstoffe, Waffen und Munition
St. Andrew's Med. Grad. Assoc. Trans.	Transactions of the St. Andrew's Medical Graduates Association
St. Barthol. Hosp. Reports	St. Bartholomew's Hospital Reports
St. Etienne, Bull. Soc. Ind. Mineral	Bulletin de la Société de l'Industrie Minerale
St. Gallen, Ber. Naturwiss. Ges.	Berichte über die Thätigkeit der St. Gallischen Naturwissenschaftlichen Gesellschaft
St. Louis, Bot. Gard. Report	Missouri Botanical Garden Report
St. Louis, Trans. Acad. Sci	The Transactions of the Academy of Science of St. Louis
St. Petersb. Acad. Sci Bull.	Bulletin scientifique publie par l'Academie Imperiale des Sciences de St. Petersbourg
St. Petersb. Acad. Sci. Compt. rend.	Compte Rendu de l'Academie Imperiale des Sciences de St Petersbourg
St. Petersb. Acad. Sci. Mem.	Memoires de l'Academie Imperiale des Sciences de St. Petersbourg
St. Petersb. Acad. Sci. Nova Acta.	Nova Acta Academiae Scientiarum Imperialis Petropolitanae
St Petersb. Acad. Sci. Recueil	Recueil des Actes des Seances Publiques de l'Academie Imperiale des Sciences de St. Petersbourg
St. Petersb. Ann Mines Russ.	Annuaire du Journal des Mines de Russie
St. Petersb. Archiv. Sci. Biol.	Archives des Sciences Biologiques publiees par l'Institut Imperial de Medecine Experimentale a St. Petersbourg
St. Petersb, Congr Bot. Bull.	Bulletin du Congres International de Botanique et d'Horticulture de St. Petersbourg le 6/18, le 8/20 et le 10/22 Mai 1869

St. Petersb. Inst. Med. Exper.	See St. Petersb. Arch. Sci. Biol.
St. Petersb. Med. Zts.	St. Petersburger Medicinische Zeitschrift
St. Petersb. Med. Wochenschr.	St. Petersburger Medicinische Wochenschrift
St. Petersb. Mem. Savants Etrang.	Memoires presentes a l' Academie Imperiale des Sciences de St. Petersbourg par divers Savants
St. Petersb. Mineral. Ges. Verh.	Verhandlungen der Russisch-Kaiserlichen Mineralogischen Gesellschaft zu St. Petersbourg
St. Petersb., Russe Geogr. Mem. (Geogr.)	Memoirs de la Société Imperiale Russe de Geographie Section de Geographie generale
St. Petersb, Russ. Geogr. Soc. Bull.	Bulletins of the Imperial Russian Geographical Society
St. Petersb. Schr. Mineral.	Schriften der in St. Petersburg gestifteten Kaiserlich-Russischen Gesellschaft für die gesammte Mineralogie
St. Petersb. Verh. Mineral. Ges.	Verhandlungen der Kaiserlich-Russischen Mineralogischen Gesellschaft zu St. Petersburg
St. Petersb. Verm. Abh.	Vermischte Abhandlungen aus dem Gebiete der Heilkunde von einer Gesellschaft pract. Aerzte zu St. Petersburg. Additional title in 1835, Medizinisch-praktische Abhandlung von Deutschen in Russland lebenden Aerzten. Continued as the Neue Abhandlung St. Petersburg
St. Quentin, Ann.	Annales Agricoles du department de l'Aisne, publiees par la Société des Sciences, Arts, Belles-Lettres, et Agriculture de St. Quentin. Annales Scientifiques, Agricoles, et Industrielles du departement de l'Aisne (Société Academique de Saint Quentin)
St. Quentin, Mem.	Memoires de la Société des Sciences, Arts, Belles-Lettres, et Agriculture de la ville de St. Quentin
St. Quentin, Seances Publ.	Société des Sciences, Arts, Belles-Lettres, et Agriculture de la ville de St. Quentin: Seances publiques.
St. Quentin, Travaux	Société Academique des Sciences, Arts, Belles-Lettres, et Agriculture de St. Quentin (Aisne)
St. Thomas's Hosp. Reports	St. Thomas's Hospital Reports
Stahl Eisen (Zts.)	Stahl und Eisen, Zeitschrift für das deutsche Eisenhüttenwesen
Stavanger Mus. Aarsber.	Stavanger Museums Aarsberetning
Staz. sper. agrar. ital.	Stazioni sperimentali agraria italiana, La
Steiermark. Geog. Mont. Ver. Ber.	Bericht des Geognostisch-montanistischen Vereins für Steiermark
Steiermark Mitth.	Mittheilungen des Naturwissenschaftlichen Vereines für Steiermark
Steiermark. Mont. Lehranst. Jahr.	Die Steiermarkisch ständische montanistische Lehranstalt zu Vordernberg
Stein, Ann.	Annalen der Geburtshülfe überhaupt und der Entbindungsanstalt zu Marburg insbesondere
Stettin, Entom. Ztg.	Entomologische Zeitung; herausg. v. d. Entomologischen Vereine zu Stettin
Steyermärk. Zts.	Steyermärkische Zeitschrift
Stirling Field Club Trans	Stirling Field Club. . . . Transactions
Stirling Soc. Trans.	Stirling Natural History and Archaeological Society. Transactions
Stockholm, Akad. Handl.	Kongliga Svenska Vetenskaps Akademiens Handlingar
Stockholm, Bihang Akad. Handl.	Bihang till Kongl. Svenska Vetenskaps Akademiens Handlingar
Stockholm Bot. Sällsk.	See Bot. Centrbl.

Stockholm Entom. För.	See Ent. Tidskr.
Stockholm, Horti Bergiani Acta	Acta Horti Bergiani. Meddelanden fran Kongl. Svenska Vetenskaps-Akademiens Trädgard Bergielund utgifna af Bergianska Stiftelser
Stockholm, Öfversigt	Öfversigt af Kongl. Vetenskaps Akademiens Förhandlingar
Stockholm Physiol. Lab. Mitth.	Mittheilungen vom Physiologischen Laboratorium des Carolinischen Medico-Chirurgischen Instituts in Stockholm
Stockholm, Svenska Läk. Sallsk Handl.	Handlingar ved Svenska Läkare-Sällskapet
Stockholm, Vet. Akad. Lefnadsteckn.	Lefnadsteckningar öfver Kongl. Svenska Vetenskaps-Akademiens efter ar 1854 aflidna Ledamoter
Stockholm, Ymer	Ymer. Tidskrift utgifven af Svenska Sällskapet för Antropologi och Geografi
Strasbourg Soc. Hist. Natur. Mem.	Memoires de la Société du Museum d'Histoire Naturelle de Strasbourg
Strasbourg Soc. Sci. Bull.	Bulletin de la Société des Sciences Naturelles de Strasbourg
Strasbourg Soc. Sci. J.	Journal de la Société des Sciences, Agriculture, et Arts, du departement du Bas-Rhin
Strasbourg Soc. Sci. Mem.	Memoires de la Société des Sciences, Agriculture, et Arts, de Strasbourg
Stray Feathers	Stray feathers. A journal of Ornithology for India and its dependencies
Stricker	See Medizin. Jahr.
Sts. Settl. P.	Straits Settlement Patent
Student	The Student and Intellectual Observer of Science, Literature, and Art
Sturgeon, Ann. Elect.	Annals of Electricity, Magnetism, and Chemistry, and Guardian of Experimental Science
Sturgeon, Ann. Phil.	Annals of Philosophical Discovery and Monthly Reporter of the Progress of Practical Science
Sucr.	La sucrerie indigene
Sucr. Belge	Sucrerie Belge, La
Sucr. ind. colon.	Sucrerie indigene et colonaile, La
Suddeut. Apoth. Ztg.	Suddeutsche Apotheker Zeitung
Suisse Soc. Zool. Ann.	See Rev. Suisse Zool.
Surveyor	Surveyor and Municipal and County Engineer, The
Sussex Natur. Hist. Soc. Proc.	See Brighton Nat Hist. Soc. Proc.
Svea	Svea. Tijdskrift för Vetenskap och Konst
Svensk farm. Tidskr.	Svensk farmaceutisk Tidskrift, Stockholm
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift
Svenska Lak. Sallsk. Forh.	Forhandlingar ved Svenska Läkare-Sällskapets Sammankomster
Svenska Mosskulturför.	Svenska Mosskulturföreningens
Svenska Sällsk. Antrop. & Geogr.	See Stockh., Ymer
Swart, Veth.	Verhandelingen en Berigten betrekkelijk het Zeewezen en de Zeewaartkunde
Swed. P.	Swedish Patent
Swiss P.	Swiss Patent
Sydney	See New South Wales
Sydney Aust. Mus. Mem.	The Australian Museum, Sydney. Memoirs
Sydney, Austral. Mus Records	Records of the Australian Museum
Symons, Meteorol. Mag.	Symon's monthly Meteorological Magazine
Tablettes Zool.	Tablettes Zoologiques

Tagbl. Frankf. Naturf.	Tageblatt Frankfurter Naturforscher
Taprobanian	The Taprobanian, a Dravidian Journal of Oriental Studies in and around Ceylon, in Natural History, Archaeology, Philology, History
Tasmania J. Natur. Sci	The Tasmanian Journal of Natural Science, Agriculture, Statistics, etc.
Tasmania P.	Tasmanian Patent
Tasmania, Roy. Soc. Monthly Not.	Monthly Notices of Papers and Proceedings of the Royal Society of Tasmania
Tasmania, Roy. Soc. Reports	Reports of the Royal Society of Tasmania
Taylor, Sci. Mem.	Scientific Memoirs, selected from the Transactions of Foreign Academies and Learned Societies and from Foreign Journals
Tech. Blatter	Technische Blätter. Vierteljahrschrift des Deutschen Polytechnischen Vereins in Bohmen
Tech. Chem. Jahr.	Technisch-Chemisches Jahrbuch (Biedermann)
Tech. Gemeindebl.	Technisches Gemeindeblatt
Technikum	Technikum des Ledermarkts
Technol.	Le Technologiste (F. Malepeyre)
Technol Quart.	Technology Quarterly
Teign Field Club Proc.	Reports of the Proceedings of the Teign Naturalists' Field Club
Tekn. Tidskr.	Teknisk Tidskrift
Telegr. Eng. J.	Journal of the Society of Telegraph-Engineers and Electricians
Telegr. J.	The Telegraphic Journal and Electrical Review
Telegr. Ver. Zts.	Zeitschrift des Deutsch-osterreichischen Telegraphen-Vereins
Temminck, Verh.	Verhandelingen over de natuurlijke Geschiedenis der Nederlandsche overzeesche bezittingen, door de leden der Natuurkundige Commissie in Oost-Indie en andere schrijvers
Termr. Füz.	Termeszetrajzi Fuzetek...Kiadja a Magyar Nemzeti Muzeum. (Natural History Magazine...published by the Hungarian National Museum)
Termt. Kózlön.	Termeszettudomanyi Kozlöny...Kiadja a K. M. Termeszettudomanyi Tarsulat. (Natural Science Papers...Published by the Royal Hungarian Natural Science Society)
Terrestrial Magn.	Terrestrial Magnetism (and Atmospheric Electricity). An International Quarterly Journal
Texas Acad. Sci. Trans.	Transactions of the Texas Academy of Science
Text. Amer.	Textile American
Text. Col.	The Textile Colorist
Text. Färb. Ztg.	Textil und Farberei-Zeitung
Text. Mfr.	The Textile Manufacturer
Text. Rec.	The Textile Record
Text. World Rec.	Textile World Record
Text. Ztg.	Textil Zeitung
Textilfreund	Der Textilfreund
Teyler's Verh.	Geologische Verhandel af Antwoord af de in 1828 uitgeschrevene en in 1830 herhaalde Prysvraag: Wat men van Geologie, etc.
Therap. Gaz.	The Therapeutic Gazette
Therap. Monats.	Therapeutische Monatshefte
Therap Neuheit	Therapeutischen Neuheiten, Leipzig
Therapist	Therapist (The) London

Thomson, Ann. Phil.	Annals of Philosophy, or Magazine of Chemistry, Mineralogy, Mechanics, and the Arts
Thomson, Archiv. Entom.	Archives Entomologiques
Thomson, Rec.	Records of General Science
Thonind. Ztg.	Thonindustrie-Zeitung
Throndhjem, Skrifter	Der Kongelige Norske Videnskabers-Selskabs Skrifter i det 19 de Aarhundrede
Tidskr. Kemi. Farm. Terapi	Tidskrfit for Kemi Farmaci Terapi
Tidskr. Mat.	Tidsskrift for Matematik
Tidskr. Mat. Fys.	Tidskrift för Matematik och Fysik, tillegnad den Svenska Elementar-Undervisningen
Tidskr. Phys. Chem.	Tidskrift for Physik og Chemi samt disse Videnskabers Anvendelse
Tiedemann, Zts.	Zeitschrift für Physiologie
Tijdschr. Entom.	Tijdschrift voor Entomologie; uitgegeven door de Nederlandsche Entomologische Vereeniging
Tijschr. Genootsch. Vis. Unita	Tijdschrift voor Genees-, Heel-, Verlos-, en Scheikundige Wetenschappen, van Wege et Genootschap: "Vis Unita Fortior," te Hoorn.
Tijdschr. Ing.	Tijdschrift van het Koninklijk Instituut van Ingenieurs
Tijdschr. nijv.	Tijdschrift ter befordering van nijverhed
Tijdstroom.	De Tijdstroom; Maandschrift gewijd van Wetenschap, etc.
Tilesius, Jahr.	Jahrbuch der Naturgeschichte zur Anzeige und Prüfung
Timehri	Timehri being the Journal of the Royal Agricultural and Commercial Society of British Guiana
Tirol, Ber. Ver. Durchf.	Bericht über die General-Versammlung des Vereins zur geogr. montan. Durchforschung des Landes Tirol, etc.
Tischl. Ztg.	Deutsche Tischlerzeitung
Tokio Univ. Mem.	Memoirs of the Science Department, University of Tokio, Japan
Tokyo Bot. Soc.	See Bot. Mag., Tokyo
Tokyo, Coll. Sci. J.	The Journal of the College of Science, Imperial University, Japan
Tokyo Geogr. Soc. J.	Journal of the Tokio Geographical Society
Tonind. Ztg.	Tonindustrie Zeitung
Töpfer Ztg.	Deutsche Töpfer und Ziegler Zeitung
Torino, Accad. Sci. Atti	Atti della R. Accademia delle Scienze di Torino
Torino, Accad. Sci. Mem.	Memoire della R. Accademia delle Scienze di Torino
Torino, Ann. Clin.	Annali Clinici
Torino, Lavori Sci. Fis. Mat.	Notizia storica dei lavori fatti dalla Classe di Scienze Fisiche e Mathematiche della R. Accademia delle Scienze negli anni 1864–65
Torino Mus. Boll.	Bollettino dei Musei di Zoologia ed Anatomia comparata della R. Universita di Torino
Torrey Bot. Club Bull.	Bulletin of the Torrey Botanical Club
Torrey Bot. Club Mem.	Memoirs of the Torrey Botanical Club
Tortolini, Ann.	Annali di Scienze, Matematiche, e Fisiche
Toulouse Acad. Sci. Bull.	Bulletin de l'Academie des Sciences, Inscriptions et Belles-Lettres de Toulouse
Toulouse, Acad. Sci. Mem.	Memoires de l'Academie des Sciences, Inscriptions et Belles-Lettres de Toulouse
Toulouse Fac. Sci. Ann.	Annales de la Faculte des Sciences de Toulouse, pour les Sciences Mathematiques et les Sciences Physiques
Toulouse Obs. Ann.	Annales de l'Observatoire Astronomique, Magnetique et Meteorologique de Toulouse.

Toulouse Soc. Hist. Natur. Bull.	Bulletin de la Société d'Histoire Naturelle de Toulouse
Toulouse Soc. Sci. Bull.	Bulletin de la Société des Sciences Physiques et Naturelles de Toulouse
Trans. Acad. Sci St. Louis	Transactions of the Academy of Sciences of St. Louis
Trans. Amer. Ceram. Soc.	Transactions of the American Ceramic Society
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society
Trans. Amer. Inst. Chem. Eng.	Transactions of the American Institute of Chemical Engineers
Trans. Amer. Inst. Homoeop.	Transactions of the American Institute of Homoeopathy, Philadelphia
Trans. Amer. Inst. Min. Eng	Transactions of the American Institute of Mining Engineers
Trans. Amer. Med. Assoc. Sec. Pharm. Therap.	Transactions of the Section on Pharmacology and Therapeutics of the American Medical Association
Trans. Amer. Micro. Soc.	Transactions of the American Microscopical Society
Trans. Amer. Soc. Civ. Eng	Transactions of the American Society of Civil Engineers
Trans Cambr. Phil. Soc.	Transactions of the Cambridge Philosophical Society
Trans. Can. Inst.	Transactions of the Canadian Institute
Trans. Engl. Ceram Soc.	Transactions of the English Ceramic Society
Trans. Faraday Soc.	Transactions of the Faraday Society
Trans. Geol. Soc. S. Africa	Transactions of the Geological Society of South Africa
Trans. Illum. Eng. Soc.	Transactions of the Illuminating Engineering Society
Trans. Inst. Brew.	Transactions of the Institute of Brewing
Trans. Jenner Inst. Prev. Med.	Transactions of the Jenner Institute of Preventive Medicine
Trans. Kansas Acad. Sci.	Transactions of the Kansas Academy of Science
Trans. Med.	Transactions Medicales; Journal de Medecine pratique
Trans. Min. Geol. Inst. India	Transactions of the Mining and Geological Institute of India
Trans. Natl Eclec. Med. Assoc.	Transactions National Eclectic Medical Association Indianapolis
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science
Transv. P.	Transvaal Patent
Trans. Path. Soc.	Transactions of the Pathological Society
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy
Trans. Roy. Soc. Can.	Transactions of the Royal Society of Canada
Trans. Roy. Soc. Edinb.	Transactions of the Royal Society of Edinburgh
Trans. Roy. Soc. London	Transactions of the Royal Society of London
Trans. Soc. Engin	Society of Engineers, Transactions
Trav. Com. Hyg. Publ.	Recueil des Travaux du Comite consultatif d'Hygiene Publique de France et des Actes Officiels de l'Administration Sanitaire
Trenton Natur. Hist. Soc. J.	Journal of the Trenton, New Jersey, Natural History Society
Treviso, Mem. Ateneo	Memorie Scientifiche e Litterarie dell' Ateneo di Treviso
Trier, Jahr.	Jahresbericht der Gesellschaft für nützliche Forschungen zu Trier
Triest Zool. Sta. Arb.	See Wien. Zool. Inst. Arb.
Trieste, Boll.	Bollettino della Societa Adriatica di Scienze Naturali in Trieste
Trieste Mus. Civ. Atti	Atti del Museo Civico di Storia Naturale di Trieste
Trieste, Program. Civ. Scuola	Programma della Civica Scuola Reale autonoma in Trieste

Trinidad Field Natur. Club J.	Journal of the Trinidad Field Nauralists' Club
Trinidad P.	Trinidad Patent
Trinidad, Proc. Sci. Assoc.	Proceedings of the Scientific Association of Trinidad
Trinidad, Sci. Assoc. Proc.	Proceedings of the Scientific Association of Trinidad
Trommsdorff, J. Pharm.	Journal der Pharmacie für Aerzte und Apotheker, und Chemiker
Tromso. Mus. Aarsh.	Tromso Museums Aarshefter
Tropenpflanzer	Tropenpflanzer (Der), Berlin
Tsch. Mineral. Mitth.	Tschermak's Mineralogische Mitteilungen
Tuberculosis	Tuberculosis. The Journal of the National Association for the Prevention of Consumption and other forms of Tuberculosis
Tübinger Blätter	Tubinger Blätter für Naturwissenschaften und Arzneikunde
Tübingen Bot. Inst. Unters.	Untersuchungen aus dem Botanischen Institut zu Tubingen
Tunis P.	Tunis Patent
Turin, Mem. Acad.	Memoires de l'Academie Royale des Sciences de Turin
Tyneside Natur. Field Club Trans.	Transactions of the Tyneside Naturalist's Field Club
U. K. Mar. Biol. Assoc. J.	Journal of the Marine Biological Association of the United Kingdom
U. S. Bur. Anim. Ind. Bull.	U. S. Department of Agriculture. Bureau of Animal Industry
U. S. Bur. Anim. Ind. Report	Annual Report of the Bureau of Animal Industry
U. S. Chief Signal Off. Ann. Report	Annual Report of the Chief Signal Officer (of the Army) to the Secretary of War
U. S. Coast Geod. Surv. Bull.	United States Coast and Geodetic Survey. Bulletin
U. S. Comm. Agric. Report	Report of the Commissioner of Agriculture
U. S. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U. S.
U. S. Dept. Agric. Report	Reports of the Department of Agriculture, U. S
U. S. Dept. Agric. Yearb.	Yearbook of the United States Department of Agriculture
U. S. Disp.	United States Dispensatory
U. S. Div. Biol. Surv. Bull.	U. S. Department of Agriculture. Division of Biological Survey. Bulletin
U. S. Div. Chem. Bull.	U. S. Department of Agriculture. Division of Chemistry. Bulletin
U. S. Div. Entom. Bull.	U. S. Department of Agriculture. Division of Entomology
U. S. Div. Entom. Insect Life	U. S. Department of Agriculture. Division of Entomology. (Periodical Bulletin.) Insect Life
U. S. Div. Entom. Tech. Ser.	U. S. Department of Agriculture. Division of Entomology. Technical Series
U. S. Div. Ornith. Mamm. Bull.	U. S. Department of Agriculture. Division of Economic Ornithology and Mammalogy. Bulletin
U. S. Div. Soils Bull.	U. S. Department of Agriculture. Division of (Agricultural) Soils. Bulletin
U. S. Entom. Comm. Bull.	Department of the Interior...Bulletin of the United States Entomological Commission
U. S. Entom. Comm. Report	(U. S.) Department of the Interior (Agriculture)... Report of the United States Entomological Commission
U. S. Fish Comm. Bull.	Bulletin of the United States Fish Commission
U. S. Fish Comm. Report	United States Commission of Fish and Fisheries. Report of the Commissioner

U. S. Geol. Surv.	United States Geological Survey
U. S. Monthly Weath. Rev.	(United States) Monthly Weather Review
U. S. Mus. Bull.	Department of the Interior...Bulletin of the United States National Museum
U. S. Mus. Proc.	Department of the Interior...Proceedings of the United States National Museum
U. S. Mus. Report	See Smithsonian Rep.
U. S. Mus. Spec. Bull.	Smithsonian Institution. United States National Museum. Special Bulletin
U. S. Naval Inst. Proc.	United States Naval Institute Proceedings
U. S. Naval Med. Bull.	United States Naval Medical Bulletin
U. S. Naval Obs. Publ.	Publications of the United States Naval Observatory
U. S. N. Amer. Fauna	U. S. Department of Agriculture. Division of Ornithology and Mammalogy. North American Fauna
U. S. P.	United States Patent
U. S. Ph.	United States Pharmacopoeia
U. S. Secty. Agric. Report	Report of the secretary of agriculture
U. S. Signal Serv. Notes	United States of America: War Department. Signal Service Notes
U. S. Signal Serv. Pap.	United States of America, War Department. Professional Papers of the Signal Service
U. S. Surv. Terr. Reports	...Annual Report of the United States Geological (and Geographical) Survey of the Territories
U. S. Weath. Bur. Bull.	U. S. Department of Agriculture. Weather Bureau. Bulletin
U. S. Weath. Bur. Report	U. S. Department of Agriculture Weather Bureau. Report of the Chief of the Weather Bureau
U. Serv. Inst. J.	Journal of the royal United Service Institution, Whitehall Yard
Udine, Relazioni	Relazioni intorno agli Atti dell' Accademia di Udine
Uhland's Tech. Rund.	Uhland's Technische Rundschau
Umschau	Umschau, Die
Ung. Naturwiss. Ver. Jahr.	Abhandlungen aus dem dritten Bande der Jahrbücher des Ungarischen naturwissenschaftlichen Vereins zu Pest, in Deutscher Uebersetzung Red. von J. Szabo
Univ. Ill. Bull.	University of Illinois Bulletin
Unters. Naturlehre	Untersuchungen zur Naturlehre des Menschen und der Thiere
Upsala, Arsskrift	Universitets Arsskrift utgifven af Kongl. Vetenskaps-Societeten i Upsala
Upsala Bot. For.	See Bot. Notiser
Upsala, Diss. Acad.	Dissertationes Academicae Upsaliae habitae
Upsala, Frey Tidskr.	Frey Tidskrift för Vetenskap och Konst
Upsala Läkareför. Förh.	Upsala Lakareforenings Forhandlingar
Upsala Naturvet. Studentsällsk.	See Bot. Centrbl.
Upsala, Soc. Sci. Nova Acta	Nova Acta Regiae Societatis Scientiarum Upsaliensis
Urug. P.	Uruguay Patent
Utrecht, Aanteek. Prov. Genoots.	Aanteekeningen van het Verhandelde in de Sectie-Vergaderingen van het Provinciaal Utrechtsch Genootschap van Kunsten en Wetenschappen
Utrecht, Ann. Acad.	Annales Academiae Rheno-Trajectinae
Utrecht, Kliniek	Kliniek: Tijdschrift voor Wetenschappenlijke Geneeskunde
Utrecht, Nieuwe Verh. Prov. Genootsch.	Nieuwe Verhandelingen van het Provinciaal Utrechsch Genootschap van Kunsten en Wetenschappen

Utrecht, Onderzoek.	Onderzoekingen gedaan in het Physiologisch Laboratorium der Utrechtsche Hoogeschool
Utrecht, Scheik. Onderzoek.	Scheikundige Onderzoekingen, gedaan in het Laboratorium der Utrechtsche Hoogeschool
Utrecht, Verh. Prov. Genootsch.	Verhandelingen van het Provinciaal Utregtsch Genootschap van Kunsten en Wetenschappen
Valais Soc Murith.	See Bull. Murith.
Valencia, Act. Med.	Actas del Instituto Medico Valenciano
Valenciennes, Mem. Soc. Agric.	Memoires de la Société d'Agriculture, des Sciences, et des Arts, de l'Arrondissement de Valenciennes
Valentin, Rep.	Repertorium für Anatomie und Physiologie
Van Diemen's Land, Roy. Soc. Papers	Papers and Proceedings of the Royal Society of Van Diemen's Land
Van Diemen's Land, Roy. Soc. Reports	Reports of the Royal Society of Van Diemen's Land (For Horticulture, Botany, and the Advance of Science)
Van Nostrand's Mag.	Van Nostrand's Engineering Magazine
Vargasia	Vargasia: Boletin de la Sociedad de Ciencias fisicas y naturales de Caracas
Varsovie Soc. Natur. Trav.	Comptes Rendus et Memoires de la Société des Naturlistes (a l'Universite Imperiale) de Varsovie
Varsovie Soc. Natur. Trav. (Mem.)	Travaux de la Société des Naturalistes de l'Univsite Imperiale de Varsovie
Vaucluse Acad. Mem.	Memoires de l'Academie de Vaucluse
Venez. P.	Venezuela Patent
Venezia, Ateneo	L'Ateneo Veneto: Rivista mensile di Science, Lettere ed Arti
Venezia, Ateneo Esercit.	Esercitazioni Scientifiche e Letterarie dell' Ateneo di Venerzia
Venezia, Atti	Atti delle Adunanze dell' I. R. Istituto Veneto di Scienze, Lettere, ed Arti
Venezia, Atti Ateneo	Atti dell' Ateneo Veneto
Venezia, Iat. Atti	Atti del Reale Istituto Veneto di Scienze, Lettere ed Arti
Venezia, Ist Mem.	Memorie del Reale Istituto Veneto di Scienze, Lettere ed Arti
Venezia, Mem. Ist Beneto	Memorie dell' I. R. Istituto Veneto di Scienze, Lettere, ed Arti
Ver. Anal. Chem.	See Repert. 'Anal. Chem.
Verh. Genootsch. Occ. Qui Non.	Verhandelingen van het Genootschap: "Occidir qui qui non servat."
Verh. Ges. deut. Naturf. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte
Verh. poly. Ges.	Verhandlungen der poltechnischen Gesellschaft
Verh. Ver. Gewerbefleis.	Verhandlungen des Vereins zur Beforderung des Gewerbefleisses in Preussen
Veröffent. kais. Gesundh.	Veröffentlichungen des kaiserlichen Gesundheitsamts
Verona, Soc. Ital. Mem.	Memorie di Matematica e Fisica della Societa Italiana della Scienze
Vet. J. London	Veterinary Journal, London
Vet. Med. Assoc. Trans.	Transactions of the Veterinary Medical Association
Veterinarian	The Veterinarian
Victoria Dept. Mines Spec. Reports	Victoria. Department of Mines. Special Reports
Victoria Field Natur. Club	See Victorian Natlist.
Victoria Inst. J.	Journal of the Transactions of the Victoria Institute or Philosophical Society of Great Britain
Victoria Natur.	The Victorian Naturalist. The Journal and Magazine of the Field Naturalists' Club of Victoria

Victoria P.	Victoria Patent
Victoria Pharm. Soc. J.	Quarterly Journal and Transactions of the Pharmaceutical Society of Victoria
Victoria Proc. Roy. Soc.	Proceedings of the Royal Society of Victoria
Victoria Trans. Phil. Inst.	Transactions of the Philosophical Institute (afterwards Royal Society) of Victoria
Victoria Trans. Roy. Soc.	Transactions of the Royal Society of Victoria
Victoria Zool. Soc. Proc.	Proceedings of the Zoological and Acclimatisation Society of Victoria
Vierteljahrschr. ärzt. poly.	Vierteljahrschrift der ärztlichen Polytechnik
Vierteljahrschr. gericht. Med.	Vierteljahrschrift fur gerichtliche Medizin und öffentliches Sanitatwesen
Vierteljahrschr. gesundheitspf.	Vierteljahrschrift fur Gesundheitspflege
Vierteljahrschr. Zahnheilk.	Vierteljahrschrift fur Zahnheilkunde
Virchow's Archiv path.	Virchows Archiv fur pathologie, Anatomie, und Histologie
Viviani, Ann. Bot.	Annali di Botanica
Voget, Notizen	Notizen aus dem Gebeite der practischen Pharmacie
Voigt, Mag.	Magazin fur den neuesten Zustand der Naturkunden, mit Rucksicht auf die dazu gehorigen Hulfswissenschaften
Vosges Soc. Emul. Ann.	Annales de la Société d'Émulation du Department des Vosges
W. Austral P.	West Australian Patent
Wag. Free Inst. Sci. Trans.	Transactions of the Wagner Free Institute of Science of Philadelphia
Wag. Jahr	(Wagner's) Jahresbericht über Chemische Technologie
Walker, Elect. Mag.	The Electrical Magazine
Warwick. Field Club Proc.	Proceedings of the Warwickshire Naturalists' and Archaeologists' Field Club
Warwick Natur Hist. Soc. Rep	Annual Reports of the Warwickshire Natural History and Archaeological Society
Washburn Obs. Publ.	Publications of the Washburn Observatory of the University of Wisconsin
Washington	Int. Med. Congr Trans., 1887
Washington	See also under U. S.
Washington Biol. Soc. Proc.	Proceedings of the Biological Society of Washington
Washington, Mem. Natl. Acad.	Memoirs of the National Academy of Sciences
Washington, Natl. Inst. Bull.	Bulletin of the Proceedings of the National Institution for the Promotion of Science
Washington Phil. Soc. Bull.	Bulletin of the Philosophical Society of Washington
Wasser Abwasser	Wasser und Abwasser
Water Supply Papers	Water Supply Papers
Watford Nat. Hist. Soc. Trans.	Transactions of the Watford Natural History Society and Hertfordshire Field Club
Weale, Quart. Papers	Quarterly Papers on Engineering
Weber, Archiv	Archiv fur die systematische Naturgeschichte
Weimer, Zts. Geburtsk.	Gemeinsame Deutsche Zeitschrift für Geburtskunde
Weinlaube	Die Weinlaube
Wernigerode Naturwiss. Ver. Schr.	Schriften des Naturwissenschaftlichen Vereins des Harzes in Wernigerode
West. Brewer	Western Brewer, The
West. Chem. Met.	Western Chemist and Metallurgist
West. Drug.	Western Druggist

Westphäl, Prov. Blätt.	Westphälische Provincial-Blätter. Verhandlungen der Gesellschaft zur Beförderung der vaterländischen Cultur in Minden
Westphäl, Ver. Jahr.	Jahres-Bericht des Westfälichen Provinzial-Vereins für Wissenschaft und Kunst
Wetter	Das Wetter. Meteorologische Montasschrift für Gebildete aller Stände
Wetterau. Ges. Ann.	Annalen der Wetterauischen Gesellschaft für die gesammte Naturkunde
Wetterau. Ges. Festgabe.	Naturhistorische Abhandlungen aus dem Gebiete der Wetterau
Wetterau. Ges. Jahr.	Jahresbericht der Wetterauischen Gesellschaft für die gesammte Naturkunde
Wetterau. Ges. Naturk. Ber.	Bericht der Wetterauischen Gesellschaft für die gesammte Naturkunde zu Hanau
Wiad. Mat.	Wiadomosci Matematyczne
Wieck's Gewerbeztg.	Deutsche Gewerbezeitung (F. Wieck)
Wied. Ann. Phys.	Annalen der Physik und Chemie (Wiedemann's)
Wied. Archiv	Archiv für Zoologie und Zootomie
Wied. Zool. Mag.	Zoologisches Magazin
Wiegmann, Archiv	Archiv fur Naturgeschichte
Wien Abh.	Naturwissenschaftliche Abhandlungen
Wien Akad. Ber.	Sitzungsberichte der kaiserlichen Akademie der Wissenschaften; Mathematisch-Naturwissenschaftliche Klasse, II Abthlg. Wien
Wien Akad. Denkschr.	Denkschriften der kaiserlichen Akademie der Wissenschaften. Mathematisch-Naturwissenschaftliche Classe
Wien Akad. Sitzber.	Sitzungsberichte der Mathematisch-Naturwissenschaftlichen Classe der kaiserlichen Akademie der Wissenschaften
Wien Almanach	Almanach der kaiserlichen Akademie der Wissenschaften
Wien Alpen-Verein, Jahr.	Jahrbuch des Oesterreichishcen Alpen-Vereins
Wien Anthrop. Ges. Mitth.	Mittheilungen der Anthropologischen Gesellschaft
Wien Anz.	Anzieger der kaiserlichen Akademie ker Wissenschaften: Math.-Naturwissensch. Classe
Wien Denkschr.	Denkschriften der Kaiselichen Akademie der Wissenschaften: Mathematisch - naturwissenschaftliche Classe
Wien Embryol. Inst. Mitth.	Mittheilungen aus dem Embryologischen Institute der k. k. Universitat in Wien
Wien Geogr. Ges. Abh.	Abhandlungen der k. k. Geographischen Gesellschaft in Wien
Wien Geogr. Ges. Festschr.	Festschrift der k. k. Geographischen Gesellschaft 1884–1898
Wien Geogr. Ges. Mitth.	Mittheilungen der k. k. Geographischen Gesellschaft in Wien
Wien Med. Chir. Acad. Abh.	Abhandlungen der k. k. medicinisch-Chirurgischen Josephs-Academie zu Wien
Wien Med. Chir. Acad. Beob.	Beobachtungen der k. k. medicinisch-chirurgischen Josephs-Academie zu Wien
Wien Naturhist. Hofmus. Ann.	Annalen des k. k. Naturhistorischen Hofmuseums
Wien Ornith. Vrr. Mitth.	Mittheilungen des Ornithologischen Vereins in Wien
Wien Phot. Corresp.	Photographische Correspondenz. Organ der Photograph. Gesellsch. in Wien
Wien Schr.	Schriften des Vereines zur Verbreitung naturwissenschaftlicher Kenntnisse

Wien Sitzber.	Sitzungsberichte der Mathematisch-naturwissenschaftlichen Classe der Kaiserlichen Akademie der Wissenschaften
Wien, Sonnblick-Ver. Jahr.	Jahres-Bericht des Sonnblick-Vereines. Wien
Wien. technol. Blätter	Wiener technologishe Blatter
Wien Ver. Naturwiss. Kennt. Schr.	Schriften des Vereins zur Verbreitung Naturwissenschaftlicher Kenntnisse in Wien
Wien, Ver. Ges. Aerzte.	Verhandlungen der k. k. Gesellschaft der Aerzte zu Wien
Wien Verh. Gewerb-Vereins.	Verhandlungen des Neiderosterreichischen Gewerb-Vereins
Wien Wochenbl. Aerzte	Wochenblatt der k. k. Gesellschaft der Aerzte in Wien
Wien Zts. Ges. Aerzte	Zeitschrift der k. k. Gesellschaft der Aerzte zu Wien
Wien, Zool. Bot. Ges. Festschr.	Festschrift zur Feier des fünfundzwanzigjahrigen Bestehens der k. k. Zoologisch-Botanischen Gesellschaft in Wien
Wien, Zool. Bot. Verh.	Verhandlungen der k. k. Zoologisch-Botanischen Gesellschaft in Wien
Wien, Zool. Inst. Arb.	Arbeiten aus dem Zoologischen Institute der Universität Wien ind der Zoologischen Station in Triest
Wiener Entom. Monatschr.	Wiener Entomologische Monatschrift
Wiener Entom. Ver. Jahr.	Jahresbericht des Wiener Entomologischen Vereins
Wiener Entom. Ztg.	Wiener Entomologische Zeitung
Wiener klin. Wochenschr.	Wiener klinische Wochenschrift
Wiener landw. Ztg	Wiener landwirtschaftliche Zeitung
Wiener Med. Wochenschr.	Wiener medicinische Wochenschrift
Wiener Mitth. Phot.	Wiener Mitteilungen (Photographischen Inhalts)
Wiener Mus. Ann.	Annalen des Wiener Museums der Naturgeschichte
Wiener Poly J.	Allgemeines Wiener polytechnisches Journal
Wiener Ztg	Wiener Zeitung
Wiener Zts. Physik.	Zeitschrift fur Physik, Chemie, und Mineralogie
Wild, Rep. Meteorol.	Repertorium fur Meteorologie, herausg. von der kaiserlichen Akad. der Wissenschaften
Wilna, Collect Med. Chir.	Collectanea medico-chirurgica Caesarea Academiae Medico-Chirurgicae cura edita
Wilts, Archaeol. Natur. Hist. Mag.	Magazine of the Archaeological and Natural History Society of Wiltshire
Wimereux Lab. (Stat.) Zool.	See Lille Inst. Zool. Trav.
Winchester, J. Sci. Soc.	Journal of Proceedings and Annual Reports of the Winchester and Hampshire Scientific and Literary Society
Wisconsin Acad. Trans.	Transactions of the Wisconsin Academy of Sciences, Arts, & Letters
Wisconsin Natur. Hist. Soc Bull.	Bulletin of the Wisconsin Natural History Society
Wisconsin Natur. Hist. Soc. Pap.	Occasional Papers of the Natural History Society of Wisconsin
Wisconsin Natur. Hist. Soc. Proc.	Proceedings of the Natural History Society of Wisconsin
Wisconsin Univ. Bull. Sci.	Bulletin of the University of Wisconsin. Science Series
Wiss. Abh. Phys.-Tech. Reichsanstalt	Wissenschaftliche Abhandlungen der Physikalish-Technischen Reichsanstalt
Wiss. Meeresuntersuch.	Wissenschaftliche Meeresuntesuchungen herausgegeben von der Kommission zur wissenschaftlichen Untersuchung der deutschen Meere in Kiel und der biologischen Anstalt auf Helgoland

Wochenbl. Archit. Ver.	Wochenblatt, herausgegeben von mitgliedern des Architekten-Vereins zu Berlin
Wochenbl. Papierfabr.	Wochenblatt der Papierfabriken
Wochensch. Brau.	Wochenschrift für Brauerei
Wochenschr. Centr.-Ver. Rubezuker-ind.	Wochenschrift des Central-Vereins für Rubenzuker-industrie in der Oesterr-Ung-Monarchie
Wochenschr. osterr. Ing. Ver.	Wochenschrift des österreichischen Ingenieur und Architekten Vereins
Wochenschr. Ver. deut. Ing.	Wochenschrift des Vereins deutscher Ingenieure
Wollen-Gewerbe	Das Deutsche Wollen-Gewerbe
Wollen Ztg.	Wollen Zeitung
Wombat	The Wombat. The Journal of the Geelong Field Naturalists' Club, and the Gordon College Amateur Photographic Association
Woods Holl Mar. Biol. Lab. Bull.	Biological Bulletin Edited by the Director and Members of the Staff, of the Marine Biological Laboratory, Woods Holl, Mass.
Woods Holl Mar. Biol. Lab. Lect.	Biological Lectures delivered at (from) the Marine Biological Laboratory (of) Woods Holl (Mass.)
Woolhope Field Club Trans.	Transactions of the Woolhope Naturalists' Field Club
Woolwich, Proc.	Minutes of Proceedings of the Royal Artillery Institution
World's Paper Trade Rev.	World's Paper Trade Review
Wunderlich, Archiv. Heilk.	See Roser und Wunderlich
Wurttemberg. Aerzt. Ver. Mitth.	Mittheilungen des Wurttembergischen Aerztlichen Vereins
Württemberg, Jahresh.	Jahreshefte des Vereins für vaterländische Naturkunde in Württemberg
Wurzburg, Arb. Bot. Inst.	Arbeiten des Botanischen Instituts in Wurzburg
Wurzburg, Arb. Phys. Lab.	Arbeiten aus dem Physiologischen Laboratorium der Würzburger Hochschule
Würzburg. Med. Zts.	Wurzburger medicinische Zeitschrift
Würzburg. Naturwiss. Zts.	Würzburger Naturwissenschaftliche Zeitschrift; Herausgegeben von der Physikalisch-Medicinischen Gesellschaft
Wurzburg Phys. Med. Festschr.	Festschrift zur Feier ihres fünfzigjahreign Bestehens herausgegeben von der Physikalisch-Medizinischen Gesellschaft zu Würzburg
Würzburg, Phys. Med. Sitzber.	Sitzungsberichte der Physikalisch-Medicinischen Gesellschaft zu Würzburg
Würzburg, Phys. Med. Verh.	Verhandlungen der Physikalisch-Medicinischen Gesellschaft
Wurzburg, Zool Inst Arb.	Arbeiten aus dem Zoologisch-Zootomischen Institut in Würzburg
Year Book Pharm.	See Brit. Pharm. Confer. Proc.
Year-book of Pharm.	Year-book of Pharmacy
Yn Lioar Manninagh	Yn Lioar Manninagh. The Journal of the Isle of Man Natural History and Antiquarian Society
Yokohama, Mitth. Deut. Ges.	Mittheilungen der Deutschen Gesellschaft für Natur und Volkerkunde Ostasiens
Yonne	See Auxere
Yonne, Bull.	Bulletin de la Société des Sciences Historiques et Naturelles de l'Yonne
Yorksh. Natur. Union Trans.	The Transactions of the Yorkshire Naturalists' Union
Yorksh. Phil. Soc. Report	Annual Report of the Council of the Yorkshire Philosophical Society

Yorksh. Proc. Phil. Soc.	Proceedings of the Yorkshire Philosophical Society
Zach, Corresp.	Correspondence Astronomique, Geographique, Hydrographique, et Statistique
Zach, Monat. Corresp.	Monatliche Correspondenz zur Beförderung der Erd- und Himmels-Kunde
Zahntech.	Die Zahntechnische Reform
Zantedeschi, Ann. Fis.	Annali di Fisica
Zeeuwsch Genootsch. Nieuwe Verh.	Nieuwe Verhandelingen van het Zeeuwsch Genootschap der Wetenschappen
Zeeuwsch Genootsch. Wet. Archief	Archief Vroegere en Latere Mededeelingen voornamelijk in Betrekking tot Zeeland, uitgegeven door het Zeeuwsch Genootschap der Wetenschappen
Zentr. Biochem. Biophys.	Zentralblatt fur Biochemie und Biophysik
Zentr. exp. Med.	Zentralblatt der experimentellen Medizin (former name Zentralblatt fur die gesamte Physiologie und Pathologie des Stoffwechsels)
Zentr. inn. Med.	Zentralblatt fur innere Medizin
Zentr. oesterr - ungar Papierind.	Zentralblatt fur die oesterr-ungar Papierindustrie
Zentr. Physiol.	Zentralblatt für Physiologie
Zentr. Physiol. Path. Stoffwech.	Zentralblatt fur die gesammte Physiologie und Pathologie des Stoffwechsels, Berlin und Wien
Zeuner, Civilingenieur	Der Civilingenieur, Zeitschrift fur das Ingenieurwesen
Ziva	Ziva: Casopis prirodnicky
Zool. Anz.	Zoologischer Anzeiger
Zool. Beitr.	Zoologische Beiträge
Zool. Bull.	Zoological Bulletin
Zool. Congr.	See Congr. Int. Zool. C. R. Int. Congr. Zool. Proc.
Zool. Jahr.	Zoologische Jahrbucher. Zeitschrift fur Systematik, Geographie und Biologie der Thiere
Zool. J.	The Zoological Journal
Zool. Soc. Proc.	Proceedings of the Scientific Meetings (General Meetings for Scientific Business) of the Zoological Society of London
Zool. Soc. Trans.	Transactions of the Zoological Society of London
Zool. Vortr.	Zoologische Vorträge
Zoologica	Zoologica. Original-Abhandlungen aus dem Gesammtgebeite der Zoologie
Zoologist	The Zoologist; a monthly Journal of Natural History
Ztg. Blechind.	Illustrierte Zeitung für Blechindustrie
Zts. Akklimat.	Zeitschrift fur Akklimatisation: Organ des Akklimatisations-Vereins in Berlin
Zts. allg. Erdkunde	Zeitschrift für allgemeine Erdkunde
Zts. allg. österr. Apoth.-Ver.	Zeitschrift des allgemeinen osterreichischen Apotheker-Vereins
Zts. allg. Physiol.	Zeitschrift fur allgemeine Physiologie
Zts. anal. Chem.	Zeitschrift für analytische Chemie
Zts. Anat.	Zeitschrift für Anatomie und Entwickelungsgeschichte
Zts. ang. Chem.	Zeitschrift für angewandte Chemie, und Zentralblatt fur technische Chemie
Zts. ang. Mikr.	Zeitschrift für angewandte Mikroskopie mit besonderer Rücksicht auf die mikroskopischen Untersuchungen von Nahrungs- und Genussmitteln, technischen Produkten, Krankheitsstoffen, etc.
Zts. anorg. Chem.	Zeitschrift für anorganische Chemie
Zts. Bauwesen	Zeitschrift für Bauwesen
Zts. Berg-Hütten Salinenw.	Zeitschrift für das Berg-Hütten und Salinenwesen im Preussichen Staate
Zts. Biol.	Zeitschrift für Biologie

Zts. Bot.	Zeitschrift für Botanik
Zts. Chem.	Zeitschrift für Chemie
Zts. chem. Apparat.	Zeitschrift für chemische Apparatenkunde (Discontinued)
Zts. Chem. Ind.	Zeitschrift für die Chemische Industrie mit besonderer Berücksichtigung der chemisch-technischen Untersuchungsverfahren 1887; later Zts. ang. Chem.
Zts. chem. Ind. Kolloide	Zeitschrift für Chemie und Industrie der Kolloide
Zts. Chemotherap.	Zeitschrift für Chemotherapie und verwandte Gebiete. (formerly Folia Serologia)
Zts. deut. geol. Ges. Abh.	Zeitschrift der deutschen geologischen Gesellschaft Abhandlungen
Zts. deut. Landw.	Zeitschrift fur deutsche Landwirthe
Zts. Dreschler	Zeitschrift für Dreschsler, Elfenbeingraveure und Holzbildhauer
Zts. Düngerw.	Zeitschrift fur Düngerwesen
Zts. Electrochem.	Zeitschrift fur Electrochemie
Zts. Entom. (Breslau)	Zeitschrift fur Entomologie im Auftrage des Vereins fur schlesische Insektenkunde zu Breslau
Zts. Ethnol.	Zeitschrift für Ethnologie
Zts. exper. Path. Therap.	Zeitschrift fur experimentelle Pathologie und Therapie, Berlin
Zts. Farben-Ind.	Zeitschrift fur Farben-Industrie
Zts. Feuerwehr.	Illustrirte Zeitschrift fur die deutsche Feuerwehr
Zts. Fischerei	Zeitschrift fur Fischerei
Zts. Fleisch. Milchhyg.	Zeitschrift fur Fleisch- und Milchhygiene
Zts. Geburtsh.	Zeitschrift fur Geburtshülfe und Frauenkrankheiten
Zts. Geburtsh. Gynäkol.	Zeitshrift fur Geburtshülfe und Gynäkologie
Zts. ges. Brauw.	Illustrirte Zeitschrift das gesammte Brauwesen
Zts. ges. Getreidew.	Zeitschrift für das gesamte Getreidewesen
Zts. ges. Naturwiss.	Zeitshrift fur die Gesammten Naturwissenschaften
Zts. Ges. Ornith.	Zeitschrift fur die gesammte Ornithologie
Zts. ges. Textilind.	Zeitschrift fur die gesamte Textilindustrie
Zts. ges. Wasserwirts.	Zeitschrift für die gesamte Wasserwirtschaft
Zts. Heilk.	Zeitschrift fur Heilkunde, als Fortsetzung der Prager Vierteljahrsschrift fur praktische Heilkunde
Zts. Hyg.	Zeitschrift fur Hygiene und Infektionskrankheiten
Zts. Immunit. Abt. I. 13. Abt. Ref.	Zeitschrift fur Immunitatsforschung und experimentelle. Therapie. Abteilung I. 13. Abteilung II. or Ref 1 vol
Zts. Induk. Abst. Vererbungslehre	Zeitschrift für Induktive Abstammungs- und Vererbungslehre
Zts. Instrumentenk.	Zeitschrift fur Instrumentenkunde
Zts. Klin. Med.	Zeitschrift fur Klinische Medizin
Zts. Krebsforsch.	Zeitschrift für Krebsforschung
Zts. Kryst. Mineral.	Zeitschrift für Krystallographie und Mineralogie
Zts. landw. Versuchsw.	Zeitschrift für das landwirtschaftliche Versuchswesen in Oesterreich
Zts. Malakozool.	Zeitschrift für Malakozoologie
Zts. Math. Phys.	Zeitschrift für Mathematik und Physik
Zts. math. Untern	Zeitschrift für mathematischen und naturwissenschaftlichen Unterrricht
Zts. Mikro. Tek.	Zeitschrift für Mikroscopischen Teknik.
Zts. Morphol. Anthrop.	Zeitschrift für Morphologie und Anthropologie
Zts. Nahr. Genuss. (Z. genuss)	Zeitschrift für Untersuchung der Nahrungs und Genussmittel, sowie der Gebrauchsgegenstände
Zts. Naturwiss.	Zeitschrift für Naturwissenshaften...im Auftrage (Organ) des Naturwissenschaftlichen Vereins für Sachsen und Thüringen

Zts. öffentl. Chem.	Zeitschrift für öffentliche Chemie
Zts. Ohrenheilk.	Zeitschrift fur Ohrenheilkunde in deutscher und englischer Sprache
Zts. österr. Ing. Ver.	Zeitschrift des österreichischen Ingenieur und Architekten Vereins
Zts. paraf. Ind.	Zeitschrift für Parafin Industrie
Zts. Parasit.	Zeitschrift für Parasitenkunde
Zts. Pflanzenkrankheiten	Zeitschrift für Pflanzenkrankheiten
Zts. physik. Chem.	Zeitschrift fur physikalische Chemie, Stöchiometrie und Verwandschaftslehre
Zts. Physik. Chem. Unterr.	Zeitschrift fur dem physikalischen und chemischen Unterricht
Zts. Physiol. Chem.	Zeitschrift fur physiologische Chemie (Hoppe-Seylers)
Zts. prakt. Geol.	Zeitschrift fur praktische Geologie
Zts. Psychol.	Zeitschrift für Psychologie und Physiologie der Sinnesorgane
Zts. ration. Med.	Zeitschrift fur rationelle Medicin
Zts. Reprodukt.	Zeitschrift fur Reproduktiontechnik
Zts. Rübenzuckerind.	Neue Zeitschrift fur Rubenzuckerindustrie
Zts. Schiess Spreng.	Zeitschrift fur das gesammte Schiess- und Sprengstoffwesen
Zts. Spiritusind.	Zeitschrift fur Spiritusindustrie
Zts. Telegr. Ver.	Zeitschrift des deutsch-osterreichischen Telegraphen-Vereins
Zts. Thiermed.	Zeitschrift fur Thiermedicin
Zts. Tuberkulose	Zeitschrift fur Tuberkulose und Heilstättenwesen
Zts. Ver. deut. Ingen.	Zeitschrift des Vereins deutscher Ingenieure
Zts. Ver. Rubenzuckerind.	Zeitschrift des Vereins fur die Rubenzucker-Industrie des deutschen Reichs
Zts. Ver. Zuckerind.	Zeitschrift des Vereins der deutschen Zuckerindustrie
Zts. Wiss. Geogr.	Zeitschrift fur wissenschaftliche Geographie
Zts. wiss. Mikro.	Zeitschrift fur wissenschaftliche Mikroscopie
Zts. wiss. Photochem	Zeitschirft fur wissenschaftliche Photographie, Photophysik, und Photochemie
Zts. wiss. Zool.	Zeitschrift fur wissenschaftliche Zoologie
Zts. Zuckerind.	Zeitschrift fur Zuckerindustrie
Zts. Zuckerind. Böhm.	Zeitschrift fur Zuckerindustrie in Böhmen
Zurich Denkschr. Med. Chir. Ges.	Denkschrift der medizinisch-chirurgischen Gesellschaft des Kantons Zurich
Zurich Mitth.	Mittheilungen der Naturforschenden Gesellschaft in Zurich
Zürich, Monats.	Monatsschrift des wissenschaftlichen Vereins in Zürich
Zürich naturf Ges.	Vierteljahrschrift der naturforschenden Gesellschaft in Zurich
Zürich Physik. Ges. Jahr.	. . . Jahresbericht der physikalischen Gesellschaft in Zürich
Zürich, Schweiz. Ges. Neue. Denkschr.	Neue Denkschriften der allgmeinen Schweizerischen Gesellschaft fur die gesammten Naturwissenschaften
Zürich, Soc. Entom.	Societas Entomologica. Organ für den internationalen Entomologenverein. Zürich
Zürich, Unters. Physiol. Lab.	Untersuchungen aus dem Physiologischen Laboratorium der Züricher Hochschule
Zürich, Verh.	Verhandlungen der Medicinisch-chirurgischen Gesellschaft des Kanton Zürich im Jahr 1826
Zürich, Vierteljahrschr.	Vierteljahrsschrift der Naturforschenden Gesellschaft in Zürich
Zwickau Ver. Naturk. Jahr	Jahresbericht des Vereins für Naturkunde zu Zwickau
Zwolle, Vooruitgang.	De Vooruitgang; Tijdschrift voor Wetenschap

CHAPTER IX.

NITROCELLULOSE THEORY.

When the celluloses in a comparatively high state of purity are brought into contact with certain organic or inorganic acids, either alone or more usually in conjunction with a dehydrating agent, union occurs, the number and nature of the combinations formed being dependent in a large measure on the anhydrous state of the cellulose, the concentration of the re-acting acid mixture, the temperature and time of contact between the cellulose and re-acting mixture, the volume and avidity of the dehydrating agent employed, and the physical condition of the cellulose molecule. Of the synthetical derivatives of cellulose, the nitric esters—the cellulose nitrates—primarily on account of their varied application in both the peaceful and warlike arts, are technically of the most importance.

Historical. The earlier investigations of the cellulose nitrates had entirely to do with those higher derivatives and explosive forms used in military operations and it was not until a much later period that the products of lower nitration—the so-called pyroxylins, collodions and photographic nitrocelluloses—and the thermo-plastic pyroxylin combinations typified by celluloid and xylonite, began to assume a commensurate industrial importance. The detailed history of the rise of the nitrocelluloses of lower nitration may perhaps be more properly considered in connection with the foundation and rise of the celluloid, lacquer, collodion and artificial silk arts, in which their commercial ramifications are so extensive at the present day.

The Xyloidine of Braconnot. The first distinct nitrocellulose compound to be described was a body discovered by Henri Braconnot in 1833, at that time professor of chemistry in Nancy[1] who prepared an inflammable, combustible and explosive body from starch, wood fiber and similar substances, by treatment with concentrated nitric acid, the body so converted being designated by the generic term of "xyloidine." This substance when washed and treated was found to explode when exposed to light and even if heated to 356° F., and also to detonate when subjected to a smart blow.[1] Braconnot describes his work as follows:

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[1] The statement is to be found that Robiquet in 1832 (Muspratt Ency. 1883, **2**, 124) treated starch with concentrated nitric acid, but am unable to corroborate. It is true that Tünnermann (Jahrb. Ch. Ph. **19**, 121; abst. Berz. Jahr. Chem. 1829, **8**, 279) distilled starch with nitric acid and obtained a new volatile acid, the nature of which is not clear. It was Berzelius who suggested the name "nitroamylin."

> "It is well known that dilute nitric acid dissolves potato starch, producing a gummy liquid very soluble in water. Quite different results, however, are obtained with concentrated nitric acid. The author has treated 5 gm. of starch with a considerable quantity of concentrated nitric acid with continuous agitation. A thick transparent liquid was obtained. This liquid, when poured into water, throws down a copious white curdy precipitate, which, when well washed and dried, weighed exactly five gm. It is white, pulverulent, tasteless, and does not redden blue litmus paper. It is colored brown by a solution of iodine. Bromine, on the other hand, has no action upon it. On boiling with water it is not dissolved, but unites together into a mass. It is not attacked nor dissolved by dilute sulfuric acid. Concentrated sulfuric acid produces a clear solution of a gummy nature, which is not precipitated by water. Concentrated hydrochloric acid dissolves it readily, especially when heated. The addition of water throws down the original material again, in an unchanged condition. Of all the vegetable acids, acetic acid alone reacts with it. It is readily soluble, especially on heating, and so much can be got into solution that the liquid becomes gummy in consistency. In contact with water a white, hard, thick coagulated precipitate is produced. On drying at a low heat a transparent material is obtained, which retains its transparency when placed in water. This thick acid liquid when applied to paper or other materials, leaves a very brilliant varnish-like coating, superior to that furnished by the best gums, whilst, at the same time it is perfectly impervious to water. Linen, coated with this material, retains its impermeability even on boiling with water. These properties show the advantages this material is able to offer in the arts. Boiling wood vinegar dissolves it, and a slight precipitate is thrown down on cooling. Neither ammonia nor caustic potash dissolves it, but they convert it into a transparent body. On boiling a brown solution is obtained, and by neutralization a precipitate is produced but slightly differing from the original materials. It is softened by boiling water without being dis-

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[1] Ann. Chim. Phys. 1833, **52,** 290; Ann. 1833, **7,** 245; Pogg. Ann. 1833, **29,** 176; Schweiger J. 1833, **68,** 368, Amer. J. Sci. 1835, **28,** 131; Berz. Jahr. 1835, **14,** 325; 1840, **19,** 437 In this connection, see Ann Chim. Phys 1833, **52,** 286; Berz. Jahr. 1835, **14,** 325; Erdmann J. 1833, **18,** 66; Ann. 1833, **7,** 242; Pogg. Ann 1833, **29,** 173. Braconnot claimed his product to be soluble in dilute boiling acetic acid, the solution so obtained being suitable for use as a lacquer.

solved, and acquires, by drying, the transparency of a gum. On exposing this material to heat it ignites with great readiness. It suffices even to heat it upon a piece of thick paper to produce rapid carbonization and liquefaction, whilst the cardboard itself, exposed to the heat, is not sensibly damaged. Heated in a small glass retort, it leaves a residue of one-sixth of its weight of carbon, difficult to incinerate, and gives a brownish liquid distillate containing much acetic acid. In contact with a solution of indigo sulfate, largely diluted with water, it is not sensibly colored blue and does not decolorize the solution. It does not show any indication of reacting with ferrous sulfate. As this material appears in some respects to resemble lignin, the author proposes for it the name of Xyloidine. Several other vegetable substances are acted on in a similar manner by the addition of nitric acid. The following observations were made on the action of concentrated acid upon lignin and gummy materials. Sawdust, when acted on by nitric acid, swells up without dissolving. On exposing the mixture to a certain temperature there is no sign of effervescence, which is very remarkable. A gummy solution is obtained so thick that it solidifies on cooling. The addition of water separates abundantly a material precisely similar to that obtained by the action of concentrated nitric acid on starch. Cotton and linen warmed with the same acid are partially dissolved, without any sensible reaction, and are converted into xyloidine. Sugar cane, mannite and milk sugar produce nothing, except in the case of the sugars, a very bitter material. Gum tragacanth, the gum arabic, inulin as well as saponin, which the author has discovered in the bark of *gymnocladus canadensis*, are by the action of nitric acid, converted into xyloidine. It is true that it is accompanied by a very bitter material from which we may conclude that these gummy materials contain sugar in some form."

This discovery apparently excited little attention and it was not until five years later that anyone took up the examination of the substances described by Braconnot, when J. Pelouze published his Memoir in the Comptes rendus in 1838.[1] He carried the investigations a step further in that he proved the presence of the nitric acid content, a point not recognized by Braconnot. Pelouze demonstrated that xyloidine would burn spontaneously when heated to 180° C., that it could also be exploded by a sharp blow or pressure and recommended it for use in the fireworks industry. He also extended his researches to the nitration of cotton, paper and vegetable substances generally, but did not take the important step of mixing sulfuric acid or other dehydrating agent with the nitric acid and, outside of theoretical generalizations, failed to make any practical application of the explosive produced by him. To the nitrocellulose produced by him he gave the name "pyroxylin."

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[1] Compt rend 1838, **7,** 713, Ann 1839, **29,** 38; J prakt Chem. 1839, **16,** 168; Berz. Jahr 1840, **19,** 437, Amer J. Pharm. 1839, **12,** 82. Compt rend 1846, **23,** 809, Annuaire Chim 1847, **3,** 454 Compt rend. 1846, **23,** 837, Annu. Chim. 1847, **3,** 454; Bibl. Univ. Arch. 1846, **3,** 273. Compt. rend. 1846, **23,** 823; Annu. Chim 1847, **3,** 454. Compt. rend. 1846, **23,** 861; Annu Chim. 1847, **3,** 454, Ann. 1847, **64,** 491. Compt. rend. 1846, **23,** 892; Berz. Jahr. 1849, **28,** 348; J. prakt. Chem 1847, **40,** 200; Annu. Chim. 1847, 454 Compt. rend 1846, **23,** 902; Annu. Chim. 1847, **3,** 454. Compt rend. 1846, **23,** 1020; Annu. Chim. 1847, **3,** 454 Compt. rend. 1847, **24,** 2; Dingl. Poly. 1847, **103,** 224; Pogg. Ann. 1847, **70,** 320; **71,** 144; Wag. Jahr. 1864, **9,** 247; Annu. Chim. 1847, **3,** 454; J. prakt. Chem. 1847, **40,** 414; Jahr. Chem. 1847–1848, **1,** 1133; J. Pharm. Chim. 1847, **11,** 297. Compt. rend. 1847, **24,** 205; Amer Jour. Sci. 1847, (2), **3,** 142, 259; Athenaeum, No. 996;

C. Bernard and L. Barreswil[1] conducted feeding experiments on domestic animals over a period of more than five years with xyloidine and although they state it is unalterable in passage through the intestines, they recommended it as a foodstuff on account of its high nitrogen content. The xyloidine with which they experimented was insoluble in water, soluble in acetic acid and in alcohol.

The experiments of Braconnot were corroborated and extended by J. de Vrij, who determined that xyloidine dissolves in acetone in considerable quantities.[2] He says, "With four grains of starch I prepared a charge for a pistol and obtained the same results as if I used six grains of ordinary sportsman's powder."

The results of E. Cottereau,[3] R. Morel,[4] Salmon,[5] Piobert,[6]

Dingl. Poly 1847, **104,** 139. Compt. rend 1848, **26,** 64 Compt. rend. 1849, **28,** 110, 146, Jahr. Chem. 1849, 472; Wag Jahr 1864, **10,** 234. Instit. No. 672, 381; abst. Berz. Jahr. 1848, **27,** 419. See also Chem. Gaz. No. 103, 56 Berz. Jahr. Chem. 1840, **19,** 438 contains the statement that Liebig had shown previous to Pelouze that nitric acid is contained in nitrated starch, the original reference of which we have been unable to locate.

[1] Compt. rend. 1846, **23,** 944.

[2] Compt. rend. 1841, **12,** 120; Compt. rend 1847, **24,** 19; Liebig and Kopp's, Ann Report. 1847–1848, **2,** 371; J. prakt. Chem. 1847, **40,** 420; Jahr. Chem 1847-1848, **1,** 1139; Watt. Dict. Chem. 1877, **5,** 410; Berz. Jahr. 1849, **28,** 348. Under the auspices of Mulder, xyloidine was investigated by C. Buijs-Ballot (Scheik. Onderzoek. Phys Lab. Utrech, 1842, **1,** 274; abst. J. prakt. Chem 1844, **31,** 309; Ann. 1843, **45,** 47; Berz. Jahr. 1844, **23,** 385; J. de Pharm. 1843, **3,** 298) who obtained a coarse, granular inflammable precipitate, readily combustible, but containing only 5.72% N. "That it contains nitric acid is seen by the manner in which it burns; whether it contains an H atom, as indicated by the number of O atoms, is undecided."

[3] Compt. rend. 1846, **23,** 1157; 1847, **24,** 205, 391, 822; Jahr. Chem. 1847–1848, **1,** 1139. J. prakt. Chem. 1847, **40,** 418; Annuaire de Chimie, 1847, **3,** 454.

[4] Compt. rend. 1846, **23,** 718, 1043; Annuaire de Chimie, 1847, **3,**

A. Gaudin,[1] Bonjean[2] and J. Fordos and A. Gelis,[3] amplified and carried a step further the results obtained by Braconnot and Pelouze and determined more perfectly the physical characteristics and chemical composition of these bodies. It was further demonstrated that the product formed by the nitration of starch is far from homogeneous. Their investigations formed an interesting prelude to the researches of Schönbein on guncotton, which together, it may be said, constitute the fundamental basis upon which the art of nitrocellulose and nitrated carbohydrates rests at the present time. It had been known before this time[4] that dilute nitric acid dissolved potato and other starches, producing a gummy liquid very soluble in water, but which had no explosive nor combustible tendencies. Braconnot by his treatment of dried starch with a considerable quantity of concentrated nitric acid with continual agitation, producing thereby a thick transparent liquid insoluble in water but readily precipitated by it, and which upon washing to neutrality and drying, gave an odorless and tasteless pulverulent mass of ready inflammability, was a distinct scientific advance. However, outside of imperfectly describing the phenomenon, he made no careful investigation of the bodies discovered by him, and his co-workers that followed up to the year 1847 apparently contented themselves with an academic investigation of the subject rather than endeavoring to place it upon any economical utilitarian basis.

Nitramidine of Dumas. J. Dumas admittedly deserves the

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454 Compt rend. 1847, **25**, 860, 914, Des Mondes, 1864, **6**, 269

[5] Compt rend. 1846, **23**, 1117, Annuaire de Chimie, 1847, **3**, 454. See also A. Seguir, Compt. rend 1846, **23**, 906. Compare Fehling, Roser and Krauss, Dingl. Poly. 1847, **103**, 220, Jahr Chem. 1847-1848, 1132.

[6] Compt. rend. 1846, **23**, 903, 1001 Annuaire de Chimie, 1847, **3**, 454

[1] Compt. rend 1846, **23**, 980, J prakt. Chem 1847, **40**, 418; Photo. Jahrbuch, **17**, 30; Bull. de la Soc d'Enc. 1847, 65; Compt rend 1846, **23**, 982, 1100; Berz Jahr. 1849, **28**, 348, 349; Annuaire de Chimie, 1847, **3**, 454. Compt. rend. 1846, **23**, 1099, Annuaire de Chimie, 1847, **3**, 154. Compt. rend. 1849, **28**, 269; Liebig, Kopp's Ann Rept 1849, **3**, 326; Dingl. Poly. 1849, **111**, 436, Poly. Centr. 1849, **15**, 686; Jahr. Chem 1848, 471.

[2] Compt. rend. 1847, **24**, 22; Jahr. Chem. 1847-1848, **1**, 1145; Liebig and Kopp's Ann. Rept. 1847-1848, **2**, 377; Annuaire de Chimie, 1847, **3**, 454. Compt. rend. 1847, **24**, 190; Jahr. Chem. 1847-1848, **1**, 1144, Liebig and Kopp's Ann. Rept. 1847-1848, **2**, 376.

[3] Compt. rend. 1846, **23**, 982; abst. Annu. de Chim. 1847, **3**, 454. In this connection see Gelis, J. Russ. Phys. Chem. Soc. 1882, **14**, I, 253; Ber. 1882, **15**, 2238.

[4] E. Mitscherlich, Pogg. Ann. 1842, **55**, 121; Berl. Ber. 1841, 379; Ann. Chim. Phys. 1843. **7**. 15· Ann 1842, **44**, 186; Taylor, Sci Mem. 1846, **4**, 1.

honor of having been the first to show that the products of the action of nitric acid upon lignin are superior in explosive energy to gunpowder. He succeeded Braconnot and Pelouze, and nitrated paper,[1] which he termed nitramidine, and which he proposed to use in the manufacture of cartridges. The same suggestion was embodied in a patent issued to J. Mollet in 1847,[2] his "zuloidine" being obtained by dissolving British gum in nitric acid. A. Dumas[3] received patent protection for a blasting fuse comprizing guncotton powdered with mercuric fulminate, and ignited by means of an electrically heated platinum wire. In conjunction with Payen,[4] J. Dumas carried on investigations on the properties of nitrated carbohydrates which seem puerile in the light of modern knowledge on the subject.

F. Pless,[5] Riotte,[6] A. Knop,[7] Karmarsch and Heeren,[8] Kaiser,[9] Lessere and Vallod,[10] Mougey,[11] Jean,[12] Balling,[13] C Combes and Flandin,[14] and L. Figuier[15] added their increment of knowledge, mostly by desultory and incoördinated experimentation. These memoirs and communications, however, aroused interest in men of reflection and mentally equipped to pursue such an investigative subject in a logical manner, and to a definite conclusion.

In 1846 R. Morel[16] gave a "private" address describing his process for the preparation of explosive cotton, and on October 12, 1847, the French Academy broke the seal on his deposited portfolio on this subject and read his note on the transformation of ligneous materials into explosives. The earlier experimenters apparently intentionally shrouded the subject with an air of mysticism, and many of the most impossible claims alleged for these nitrated products were readily accepted *in toto*, and were not challenged nor refuted until many years after. The patent of Morel in this subject[1] is a hazy, rambling document, replete with abstruse phraseology and abounding in hopes of what might be accomplished, rather than a clear exposition of what had been done. He used carded cotton, nitric acid and water.

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[1] Compt rend 1846, **23,** 806, 983, Annuaire de Chimie, 1847, **3,** 454, Amer J Sci. 1847, (2), **3,** 251, L'Institute, Dec 2, 1861, No 674

[2] E P 11657, 1847, abst Mechan. Mag **47,** 419

[3] E P 2100, 1864

[4] Bull Soc. d'Enc 1846, 619, 620, 621

[5] Bayer, Gwbl 1846, 349, 391; 392.

[6] Compt. rend 1846, **23,** 1090

[7] Chem Centr. 1849, **20,** 801, 1850, **21,** 49, Ann 1850, **74,** 347, J prakt Chem. 1849, **48,** 362, 1850, **49,** 228, Jahr Chem 1849, **2,** 466, Chem Gaz 1850, 81, Compt rend 1846, **23,** 808, Dingl Poly 1846, **102,** 165 A and W. Knop, J prakt Chem. 1849, **48,** 362, 1852, **56,** 334; Chem Gaz. 1850, 81; Ann 1850, **74,** 347, Pharm. Centr 1852, **23,** 129, 423, Jahr. Chem. 1852, **5,** 657.

[8] Dingl. Poly 1846, **102,** 165

[9] Gwbl. 1846, 349, 391, 392; Bayer Kunst u Gewerbl. 1846, 665, 739; 1847, 35 Wieck's Gwz 1864, 22.

[10] Compt rend 1846, **23,** 932, 974

[11] Compt. rend. 1846, **23,** 879; Annuaire de Chimie, 1847, **3,** 454.

[12] Compt. rend. 1847, **24,** 877, 1053; abst Jahr Chem 1847–1848, **1,** 1140; Liebig Kopp's Ann. Rept. 1847–1848, **2,** 373.

[13] Zschr. d. Gwbw. 1846, 911.

[14] Compt rend 1846, **23,** 940. Compt rend. 1846, **23,** 1090; Annuaire de Chimie, 1847, **3,** 454,

[15] Compt. rend. 1846, **23,** 1090, Annuaire de Chimie, 1847, **3,** 454.

[16] Compt rend. 1846, **23,** 718, 1043; Annuaire de Chimie, 1847, 454. Compt rend. 1847, **25,** 860, 914. Des Mondes, 1864, **6,** 269.

Salmon[2] preferred sulfuric acid and potassium nitrate; E. Cottereau[3] employed sulfuric acid as a "dehydrating" agent, while Becker[4] disclosed his process for preparing a cotton powder "whose energy surpassed all the analogous products which could be compared to it." Arago[5] entertained the French Academy by relating, in 1846, experiments on "fulminating cotton," in which the ball of a Roberts gun, with a charge of 0.35 gm. penetrated 14 mm. of a wooden plank situated at a distance of 11 m.

M. Pettenkofer,[6] W. Grove,[7] entered the field, but contributed only generalizations. Due to the rather capricious action of this nitrated product and the frequent tendency to explode without apparent provocation, experimenters became cautious. Bonjean[8] proposed to dye this product pink with Dandle wood extract, in order to avoid mistakes, a little alum being added to increase the intensity of the color and the effectiveness. A. Seguier, assisted by Clerget,[1] determined the comparative ballistics of the "paper of Pelouze," and found the brisant augmentation always greater than gunpowder but decidedly erratic. Colonel O. Averos[2] carried out a research authorized by the "high commissioner of explosives in Paris," and investigated all the known methods of nitrocellulose formation which had been proposed up to that time. The Colonel's voluminous report as a *parvum in multo* is a classic, and should repose in every nitrocellulose antiquariat's library.

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[1] F. P 3280, Oct 3, 1846, addn dated Oct 6, 8, 26, Nov. 30, 1846. F P 3281, Oct 14, 1846 See his F P 2333, Aug 17, 1846 Morel and Chaudun, F P 3282, Nov 3, 1846

[2] Compt rend 1846, **23,** 1117, Annuaire de Chimie, 1847, **3,** 454

[3] Compt rend 1846, **23,** 1157, J prakt Chem 1847, **40,** 418; Annuaire de Chimie, 1847, **3,** 454. Compt rend 1847, **24,** 205, 391, 822. Jahr. Chem 1847–1848, **1,** 1139

[4] Compt rend 1846, **23,** 983, Annuaire de Chimie, 1847 **3,** 454.

[5] Compt rend 1846, **23,** 718, 879

[6] Dingl Poly. 1846, **102,** 445, Bayer Kunst. Gewerbl 1846, 57 Compt rend. 1846, No. 18, 19, 21; Dingl Poly 1847, **103,** 42, 48 Bayer Kunst Gew. Blatt. Jan. 1847, Dingl Poly 1847, **103,** 209, 219, Liebig, Kopp Ann Rep 1847–1848, **2,** 367; Jahr Chem 1847–1848, **1,** 1133 Chem. Centr. 1847, **18,** 63.

[7] Dingl. Poly. 1846, **102,** 86. See also, H. Bohl, Dingl. Poly 1849, **112,** 236, Technologiste, April, 1849.

[8] Compt. rend. 1847, **24,** 22; Jahr Chem 1847–1848, **1,** 1145; Liebig and Kopp's Ann Rept. 1847–1848, **2,** 377; Annuaire de Chimie, 1847, **3,** 454. Compt. rend. 1847, **24,** 190; Jahr Chem 1847–1848, **1,** 1145; Liebig and Kopp's Ann. Rept. 1847–1848, **2,** 376.

Schönbein and Guncotton. The various proposals which had been made previous to the announcement of the discovery of guncotton by Schönbein in 1846 did not meet with extended favor, as it had been impossible up to that time to produce a uniform material or to render the same sufficiently stable. Notwithstanding the fierce polemics which were indulged in after the announcement of the discoveries of Schönbein between himself and the members of the French Academy on one side, and Otto, Böttger and German co-workers on the other, due in a great measure to the attempts to keep the manufacturing details of his process secret while patents thereon were pending, the fact must be recognized that an entirely new stage in the history of pyroxylin was initiated when Christian Frederick Schonbein, in 1845,[3] announced that he had discovered a method whereby cotton could be converted into a very explosive body by treatment with nitric acid for a short time, and that no observable structural changes accompanied this reaction.

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[1] Compt. rend. 1846, **23,** 862, 906, 1047, Annuaire de Chimie, 1847, **3,** 454; Majocchi, Ann. Fis Chim 1847, **25,** 116.

[2] Compt. rend 1846, **23,** 874; Annuaire de Chimie, 1846, 454, Tech. Mitth. Elsner, 1846-1848, 124, J prakt Chem 1847, **40,** 193, 257.

[3] Memoir No 69 Pogg. Ann 1843, **59,** 240; Archives de l'Electr. 1843, **3,** 295, Munchen, Abhandl 1837–1847, **3,** 587. No. 70. Archives de l'Electr. 1844, **4,** 56, Basel, Ber. 1844, **6,** 12, Pogg Ann. 1844, **62,** 220. No 71. Archives l'Electr. 1844, **4,** 333. No 72. Atti Scienz. Ital. 1844, 167. No 75. Basel, Ber 1844, **6,** 10 No 77. Bern, Mittheil. 1844, 109. No 78 Pogg. Ann. 1844, **63,** 406; Bibl. Univ 1844, **52,** 358 No. 79. Pogg. Ann. 1844, **63,** 520. No 80. Proc. Roy. Soc. 1844, **5,** 507. No. 82. Archives de l'Electr. 1845, **5,** 11, 337; Pogg. Ann. 1845, **65,** 69; 1846, **67,** 78. No. 83. Archives de l'Electr. 1845, **5,** 342 No. 84 Arch. de l'Electr. 1845, **5,** 556; Chem. Soc. Mem. 1845–1848, **3,** 2; Phil Mag. 1846, **28,** 432, Pogg Ann. 1846, **67,** 225. No. 85. Brit. Assoc. Rep. 1845, 91. No. 87. J. prakt. Chem 1845, **34,** 492. No 89. Milano, Giorn. 1st. Lomb. 1845, **6,** 200. No. 90. Phil. Mag. 1845, **27,** 386. No. 91. Pogg. Ann. 1845, **65,** 161. No. 92. Pogg. Ann. 1845, **65,** 197. No. 93. Pogg. Ann. 1845, **65,** 190. No. 94. Pogg. Ann. 1845, **65,** 196. No. 95. Pogg. Ann. 1845, **66,** 291; Phil. Mag. 1845, **27,** 450. No. 96. Pogg. Ann. 1845, **67,** 89. No. 98. Proc Roy. Soc. 1845, **5,** 543. No. 99. Proc. Roy. Soc. 1845, **5,** 565. No. 103. J. prakt. Chem. 1846, **37,** 129. No. 105. J. prakt. Chem.

So much has been loosely written on this subject—apparently often by those who have not taken the pains to critically examine the original scientific repositories, that the steps leading up to this discovery, as well as the attitude assumed by Schönbein in relation to certain claims put forward by Pelouze and other Academicians as regards priority, may perhaps be best understood by reference to the original communication of Schönbein as follows:[1]

"The substance to which I have given in German the name *Schiesswolle*, and in English that of guncotton, having excited a lively curiosity, it may be interesting to the scientific world to become acquainted with some details of the way in which I was

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1846, **37,** 144, Basel, Ber 1847, **7,** 22 No 106 J prakt. Chem. 1846, **39,** 370 No 107. Phil Trans 1846, 137 No 111 Pogg Ann. 1846, **67,** 211. No 112 Pogg Ann 1846, **67,** 217, Basel. Ber 1847, **7,** 9. No 113. Pogg Ann 1846, **68,** 42, Basel, Ber 1847, **7,** 23 No 114 Pogg. Ann. 1846, **68,** 159 No 115 Oefversigt, 1846, **3,** 93 No 117. Basel, Ber. 1847, **7,** 6 No 118 Basel, Ber 1847, **7,** 7 No 119. Basel, Ber. 1847, **7,** 13 No 120 Basel, Ber 1847, **7,** 14. No 121. Basel, Ber. 1847, **7,** 15. No 122 Basel, Ber 1847, **7,** 17. No 124 Bibl Univ. Arch. 1847, **4,** 20; Majocchi, Ann. Fis Chim. 1847, **25,** 159, Phil Mag. 1847, **31,** 7. No. 126. J prakt Chem 1847, **41,** 225, Schweizer, Gesell. Verhand 1847, 68. No. 128 Pogg. Ann 1847, **70,** 87. No 129 Pogg Ann. 1847, **70,** 100. No. 130 Pogg Ann 1847, **71,** 517 No 131 Pogg. Ann. 1847, **72,** 466. No. 132. Schweizer Gesell Verhand 1847, 73, Pogg Ann. 1847, **77,** 450. No. 136 Amer J. Sci 1847, **4,** 320. No. 142 Pogg Ann 1848, **75,** 361. No 146 Schweizer, Gesell. Verhand 1848, 114, Pogg Ann. 1848, **75,** 367. No. 147 Basel, Ber 1849, **8,** 3 No 148 Basel, Ber. 1849, **8,** 5. No. 149. Basel, Ber 1849, **8,** 6 No. 150 Basel, Ber. 1849, **8,** 8. No. 151. Henle und Pfeufer, Zts 1849, **7,** 185. No 152 Schweizer, Gesell. Verhand. 1849, 98, Pogg. Ann 1849, **78,** 289, Bibl Univ Arch. 1850, **13,** 192 No. 153. Schweizer, Gesell. Verhand. 1849, 116; Pogg Ann. 1849, **78,** 162. No 154 Schweizer, Gesell Verhand 1849, 126 No 157. J prakt. Chem. 1850, **51,** 30; J Pharm (de), 1851, **19,** 385. No 160. J. prakt. Chem. 1851, **53,** 248 Schonbein wrote to Berzelius concerning this discovery on March 5, 1846 (C Kahlbaum, "Briefwechsel Berzelius-Schönbein," p. 80), and to M. Faraday, Feb 27, 1846 (C Kahlbaum, "Letters of Faraday and Schonbein," 1899, p. 152). Pogg Ann 1847, **70,** 100; Berz. Jahr. 1848, **27,** 424; 1849, **28,** 358, Jahr. Chem 1847–1848, **1,** 1128, 1146; Arch. ph. Nat. **4,** 20; Chem. Centr 1847, **18,** 505; Phil Mag 1847, (3), **31,** 7; Phil. Trans. 1846, **136,** 137, Bibl. univers (4), **3,** 18; Ann Sci phys. nat **4,** 20, 28; Am. J Sci. 1847, (2), **4,** 138, 440; Liv. Edin. and Dub. Phil. Mag. **31,** 7; Mining J., Apr 10, 1847. Dingl. Poly. 1846, **102,** 86, 1847, **104,** 139; Compt. rend. 1846, **23,** 678; Annu. Chim. 1847, **3,** 454; Pharm. J. Trans. **6,** 189, 533. Memoir No. 129. Dingl. Poly. 1862, **166,** 313. Augs. Allg. Ztg. Oct. 5, 1846. Liebig, Kopp's Ann. Rep. 1847–1848, **2,** 363, 374, 377, 378. Sci. Amer., March 28, 1863. The Engineer, June 19, 1874. Zts. Schiess. Spreng. 1912, **7,** 164.

1. For considerable data contained in this topic, acknowledgment is due to Historical Papers on Modern Explosives, G. MacDonald, 1912.

irst led to its discovery. The results of my researches on ozone ed me, in the last few years, to turn my attention particularly o the oxides of nitrogen and principally to nitric acid. The umerous experiments which I have made on this subject have ed me, as I have stated in detail in *Poggendorff's Annalen*, to dopt a peculiar hypothesis of the so-called hydrates of nitric cid, sulfuric acid, etc., as well as the normal nitrates, sulfates, tc. For a long time I have entertained doubts as to the existence of compound bodies of this nature, which cannot be isolated, and which are stated to be capable of existing only in combination with certain other substances. For a long time, also, I had come to the conclusion that the introduction of these imaginary combinations had only been an apparent progress in theoretical chemistry, and that it had even impeded its development. It is well known that what has most contributed to the admission of the existence of these compounds has been the opinion, generally received among chemists, respecting the nature of nitric acid. (Here follows a discussion on the constitution of nitric and sulfuric acids.) My experiments on ozone have shown that this body forms a peculiar compound with olefiant gas, without apparently oxidizing in the least either the hydrogen or the carbon of the gas. I had an idea that it would not be impossible that certain organic matters, exposed to a low temperature, would likewise form compounds, either with ozone alone, which, on my hypothesis, occurs in a state of combination or mixture in the acid mixture, or with NO_4. It was this conjecture (doubtless very singular in the eyes of chemists) which principally led me to commence experiments with common sugar. I made a mixture of 1 volume of nitric acid (1.5) and 2 volumes of sulfuric acid (1.85) and cooled the mixture to 0° C. I then added some finely powdered sugar so as to form a paste. I stirred the whole and at the end of a few minutes the saccharine substance formed itself into a viscous mass, entirely separated from the acid liquid, without any disengagement of gas. The pasty mass was washed with boiling water until the latter no longer showed any acid reaction; after which I deprived it as much as possible, at a low temperature, of the water which it still retained. The substance now possessed the following properties: Exposed to a low temperature it is hard and brittle; at a moderate temperature it may be moulded like jalap resin, which gives it a beautifully silky luster. It is semi-fluid at 100° C.; at high temperatures it gives off red vapor. Heated still more, it suddenly deflagrates with violence, without leaving any perceptible residue. It is almost insipid and colorless, transparent like the resins, almost insoluble in water, but easily soluble in essential oils, ether and concentrated nitric acid, and in most cases it acts in general like the resins from the chemical and physical point of view. Friction, for instance, renders it electrical. It should be added that the acid mixture by means of which this resinous body was obtained, has an extremely marked bitter taste. I wished to make experiments also with other organic substances, and I soon discovered, one after another, all those about which there has been so much said of late in the French Academy. All this occurred in December, 1845, and the first few months of 1846 In March I sent specimens of my new compound to some of my friends, especially Faraday, Herschel and W. Grove. It is necessary to note expressly that guncotton formed part of these products, but I must add that hardly was it discovered, when I employed it in shooting experiments, the success of which encouraged me to continue them. Accepting the obliging invitation which I received, I went to Wurtenburg, in the middle of April, and made experiments with guncotton, both in the Arsenal at Ludwigsburg, in the presence of artillery officers, and Stuttgart before the King himself. In the course of May, June and July, with the kind cooperation of Commandant de Mechel, M. Burkhardt, captain of artillery, and other officers, I subsequently made in Bâle, numerous experiments with arms of small caliber, such as pistols, carbines, etc., and afterwards with mortars and cannon, experiments at which Baron de Krüdener, the Russian Ambassador, was several times present. I may be allowed to mention that I was the person who fired the first cannon loaded with guncotton and shot, on July 28, 1846, after we had previously ascertained by experiments with mortars that the substance in question was capable of being used with pieces of large caliber. About the same time, and independently, I employed guncotton to blast some rocks at Istein, in the Grand Duchy of Baden, and to blow up some old walls at Bâle, and in both cases I had opportunities of convincing myself in the most satisfactory manner, of the superiority of this new explosive over gunpowder. In July I also made the first capsules and employed them with success for muskets in the presence of the abovenamed officers. Experiments of this kind, which took place frequently and in the presence of a great number of persons, could not long remain unknown, and the public journals soon gave, without participation on my part, descriptions more or less accurate, of the results which I obtained. This circumstance, joined to the short notice which I inserted in the May number of the *Poggendorff's Annalen*, could not fail to attract the attention of German chemists. In the middle of August I received from Böttger, Professor at Frankfort, the news that he had succeeded in preparing guncotton and other substances. Our two names thus became associated in the discovery of the substance in question. To Böttger, guncotton must have been particularly interesting, as he had previously discovered an organic acid which deflagrated readily. In August I went to England, where, assisted by the able engineer, Richard Taylor of Falmouth, I made numerous experiments in the mines of Cornwall, which were entirely successful in the opinion of all competent witnesses. Experiments on the action of guncotton were also made in several parts of England under my directions, both with small firearms and pieces of artillery, and the results obtained were very satisfactory. Until that time there had been little or nothing said of guncotton in France; and it would appear that the short notice which W. Grove gave at Southampton, at the meeting of the British Association, and the experiments with which he accompanied them, first served to attract the attention of French chemists to this substance. At Paris the thing was at first considered hardly credible, and jokes even were passed upon it. But when there could no longer remain any doubt as to the reality of the discovery, and when several chemists in Germany and other countries had published the processes which they employed to prepare guncotton, then a lively interest was manifested in a subject which had just before excited derision, and it was soon pretended that the new explosive was an old French discovery. It was declared to be nothing more than the xyloidine first discovered by Pelouze, and the only merit left to me was to have conceived the happy idea of putting this substance into a gunbarrel. The knowledge of the composition of xyloidine ought to have sufficed to have convinced those who put forward that opinion that it is not suited for firearms on account of its containing too much carbon and too little oxygen, for the chief part to be converted during the combustion into gaseous matters. It was, moreover, very easy to discover the essential differences which exist between xyloidine and guncotton. Nevertheless the error was kept up for some months. Matters stood thus when on November 4th last, a Scotch chemist, Walter Crum of Glasgow, published a memoir in which he showed that guncotton is not the same product as xyloidine, but that it presents an essentially different composition, and towards the end of the same month the French Academy received a communication of the same nature. The guncotton was no longer xyloidine, it was called *pyroxyline*, and the first was admitted to be unsuitable for firearms. If, therefore, it is proved that from the commencement of 1846 I prepared guncotton and applied it to the discharge of firearms and that Böttger did the same in August—if it be admitted that xyloidine cannot serve the same purpose as guncotton, and if it be notoriously known that what is now called pyroxyline was not brought before the French Academy and the world until towards the middle of November last, the idea of attributing to France the discovery of guncotton cannot be seriously entertained, or of assigning to me merely a practical application of that which another had discovered. I appeal to the justice of Frenchmen to decide the point to whom belongs the honor, of not only being the first to apply the new substance in question, but also of having first prepared it—to Braconnot and Pelouze or myself. I must, moreover, add expressly that it was not xyloidine even, which led to my discovery, however intimate may be its relations with guncotton. It was theoretical ideas, possibly very erroneous ones, but which are peculiarly my own, as well as some facts which I was also the first to discover. *Suum cuique* is a principle of morality on which society at large rests; why should it not be strictly respected in the domain of science? Pelouze is a distinguished chemist and already possesses a sufficiently high reputation, not to require to elevate his pretensions on the merits of others; and I am fully persuaded that this esteemed chemist, of well known truth of character, will, approaching with impartiality the circumstances which have occurred, freely render me the justice to which I consider myself entitled."

A patent had been applied for in England in the name of J. Taylor,[1] and in the United States under his own name but assigned to W. Robertson.[2] In the United States patent he clearly shows his method of formation, as appears from the following description:

"Treating vegetable fibrous substances and other organic matters being of a chemical composition analogous to that of the said vegetable fibrous substances with a mixture of nitric acid of 1.5 specific gravity, or thereabout, and sulfuric acid of 1.85 specific gravity, or thereabout, at the common temperature, or a lower one, by which compounds are formed which on being heated more or less ignite suddenly and produce gaseous matters. Of all the vegetable substances known to me, cotton-wool is the most fit material for producing an explosive compound answering the purposes of gunpowder, and I therefore claim the use of cotton-wool for this purpose when prepared as herein directed.

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[1] E. P. 11407, 1846; abst Rep Pat Inv. 1847, **9**, 292; Mechan Mag. **45**, 393; **46**, 358, Jahr. Chem 1847–1848, **1**, 1142, Dingl. Poly. 1847, **104**, 450; Eng. and Architect's J. **10**, 142; Lond. J **29**, 280. In this same year he also entered into negotiations with Messrs John Hall & Sons, of Faversham, and on October 13th an agreement was made for the erection of a factory for the manufacture of guncotton

In 1847 Messrs. John Hall & Sons erected the factory, but it was destroyed by a very disastrous explosion on July 14th of the same year and never rebuilt. This disaster appears to have acted as a deterrent to the manufacture of guncotton in England because for the next 16 years very little further work was done in that country.

All the guncotton not involved in the explosion at Faversham was buried. In 1864 Abel received a sample of the disinterred guncotton, and he found that the material did not appear to have undergone any change. It was readily soluble in ether-alcohol and had a nitrogen content of about 12% (Trans. Roy Soc. 1867). This old-time guncotton was again examined as late as 1909, this time by G. W. MacDonald, who reported his findings at the Inter. Congress App. Chem. 1909. The sample tested was disinterred about 1873, and since that date had been stored in a bottle. The material was in good condition, quite stable, had a nitrogen content of nearly 12% and was 89% soluble in ether-alcohol.

[2] U. S. P. 4874, 1846; abst. Pharm. J. Trans. **6**, 533.

To produce that explosive compound the following process is to be gone through.

First. Clean cotton is immersed in a mixture containing the nitric and sulfuric acids of the specific gravities before mentioned. As to the ratio of volumes in which the two acids are to be mixed, it may vary to a considerable extent, and the specific gravity may vary also; but the above is preferable. The ratio, however, yielding the best results is that of one volume of nitric acid to two or three of sulfuric acids.

Second. Into a mixture of the acids of the last-named description clean cotton is plunged in such a manner as to be entirely impregnated by the said acid mixture. Care must be taken that the temperature of the said acid mixture be not above 50° or 60° Fahrenheit.

Third. The cotton, after having remained for an hour or two (more or less) in contact with the acid mixture, must be subject to pressure in order to remove as much as possible from the cotton the acid particles. That being done, the pressed cotton is to be washed as long until the acid is entirely removed. That operation being finished, the prepared cotton is to be dried in moderately heated rooms. Before using the dry cotton it is important to card it.

Fourth. Cotton-wool acquires also a high inflammability and explosive power by exposing that material at the common temperature to the action of pure nitric acid of the greatest specific gravity that acids can be prepared. This way of rendering the cotton inflammable appears to be less easy and economical than the method above described; but the use of this cotton-wool so prepared I claim as part of my discovery.

Fifth. For many purposes it is good to impregnate the explosive cotton by some nitrate of potash. This preparation imparts to the cotton the property of disengaging a more intense light than the pure prepared cotton does, and the use of nitrate potassa or other known chemical substitutes I claim in combination with the acid treatment."

Schönbein gave the product described and patented by him the name of *schiesswolle* or *schiessbaumwolle* in German, or *guncotton*, in English, and made successful tests with it for shooting and blasting. For pecuniary reasons Schönbein did not disclose the results of his investigations in detail, and meanwhile others had quietly been taking up the subject, and their results appeared about the same time as the communications of Schönbein.

Apparently entirely independently, Böttger of Frankfort, experimenting along similar lines, also announced the preparation of an explosive cotton in August, 1846, and described in generalities its ballistic properties, and uniting his efforts with Schonbein, presented the results of their discoveries to the German Union. The latter, stipulated, however, that before the prize which had been offered for such an invention could be awarded, it was incumbent upon the inventors to demonstrate to the satisfaction of the representatives of the Union, that the new substance was the equal, or superior to gunpowder, and would be able to satisfactorily replace the latter in all respects. A Commission was appointed to test the guncotton, and the publication of the manufacturing methods was held in abeyance, pending the report of this Commission.

Meanwhile, in an unobtrusive manner,[1] F. Otto, of Brunswick, had been pursuing this subject, and published in the Augsburger Allgemeinen Zeitung of October 5, 1846, that he had succeeded in producing an explosive cotton similar to the Schonbein guncotton, by immersing cleaned cotton for about one-half minute in very highly concentrated nitric acid, followed by careful washing and drying.

The three-sided and vitriolic controversy that immediately followed the publication of Otto created widespread interest among investigators, and attempts were begun upon all sides in systematic endeavors to improve the Otto method (the only rational method of nitrocellulose manufacture *published* up to this time), and to render the guncotton more stable and less brittle.

R. Böttger, having found[2] that the "pure" nitrocellulose was completely soluble in sodium stannite solution, from which cellulose may be regenerated by acidifying, proposed the use of the new body as an excellent filtering material for mineral acids,[3]

[1] Zts d. Gwbw. 1846, 859; Hannover Ztg Oct 6, 9, 1846. Dingl. Poly. 1864, **102**, 153, 154. Deut. Allgem Ztg. 1846, Oct 5, J. prakt Chem. 1847, **40**, 193; Compt. rend. 1846, **23**, 807, Dingl Poly 1846, **102**, 164, 168, 331, 408

[2] Jahr. phys. Verein Frankfurt a/M 1872-1873, Chem Centr. 1874, **45**, 374; J. C. S 1874, **27**, 192, 1078; Dingl Poly 1873, **209**, 315, Deut. Ind. Ztg. 1873, 18; Wag Jahr. 1873, **19**, 356; Poly. Centr 1873, **39**, 268; Jahr. Chem 1873, **26**, 827, Indblatter, 1873, No 1, Elsner-Mitth 1872-1873, **22**, 231.

[3] R. Bottger, Ann. 1860, **114**, 111; Poly. Notiz. 1860, **15**, 97, Dingl

and showed that, whereas cotton is ignited in contact with a mixture of potassium permanganate and concentrated sulfuric acid, guncotton and gunpowder are not affected.[1] He prepared red colored fuses or quick matches[2] from guncotton by nitrating loosely spun twine or rope, which was afterwards immersed in an alkaline solution of fuchsine. In conjunction with Schönbein,[3] a memoir on the subject was published in 1847, and the prize was finally awarded to them.[4]

The announcement in the French Academy of the discoveries of Schönbein aroused a remarkable interest and brought forth a large number of communications on the subject. A. Gaudin contributed several memoirs,[5] and found that "the preparation of pyroxylin is not always successful when nitric acid is employed according to the method described by some eminent chemist at great detail," but found that a satisfactory stability was obtained when the nitrated cotton was dried in a special chamber with revolving racks and cold air circulation, in an apparatus as devized by *him*.

E. Peligot[6] made careful combustions of cotton nitrated with equal parts of fumic nitric and sulfuric acids, from which he

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Poly. 1860, **155,** 463; J prakt. Chem. 1860, **79,** 384; Jahr Chem 1860, **13,** 680; Poly. Centr. 1860, **26,** 863; Bull. de la Soc Encour. 1860, 698; Repert de Chim. appl. II, 186; Verhandl des niederosterreich Gewerbevereins. 1860, 75, Jahr. Pharm. **14,** 179, Wag. Jahr. 1860, **6,** 466, Amer. J. Sci. 1860, (2), **30,** 268; Proc Amer. Pharm Assoc 1860, **9,** 96. Jahr. phys Verein Frankfurt a/M. 1872–1873, 10; Chem Centr 1874, **45,** 346.

[1] Pogg. Ann Jubelband, 1874, 156; N. Rep. Pharm **23,** 177; abst. Jahr. Chem. 1874, **27,** 270

[2] Poly. Notiz 1873, **28,** No 1; Dingl Poly. 1873, **207,** 261; Poly. Centr. 1873, **39,** 267; Chem. Centr. 1873, **44,** 107; Amer. Chem 1873, 397; Wag. Jahr. 1873, **19,** 355; Chem. Teck. Rep. 1873, **13,** I, 189; Pharm. Centrahl. 1873, No. 10; Elsner, Mitth. 1872-1873, **22,** 300; J. C. S. 1873, **26,** 956; Jahr. Chem. 1873, **26,** 1032. Ber. 1876, **9,** 1795; Jahr. phys. Ver. Frank 1877–8, 25; Chem. Centr. 1879, **50,** 750.

[3] Pogg Ann. 1847, **70,** 320; Berz. Jahr. 1849, **28,** 247, 351; Jahr. Chem. 1847–1848, **1,** 1143; Augsb. Allg. Ztg. 3 Jan., 1847, Suppl. page 21; Dingl. Poly. 1847, **103,** 220; Arch. ph. Nat. **4,** 20, 28; Compt. rend. 1846, **23,** 678; Liebig, Kopp's Ann. Rep. 1847–1848, **2,** 367, 375; Bibl. Univ. Archives, 1847, **4,** 28.

[4] Dingl. Poly. 1846, **102,** 167.

[5] Compt rend. 1846, **23,** 980, 1099; J. prakt. Chem. 1847, **40,** 418; Photo Jahr. B. **17,** 30; Bull de la Soc. d'Enc. 1847, 65; Compt. rend. 1846, **23,** 982; Berz. Jahr. 1849, **28,** 348, 349; Annuaire de Chimie, 1847, **3,** 454; Berz. Jahr. 1849, **28,** 349. Compt. rend. 1849, **28,** 269; Liebig, Kopp's Ann. Rept. 1849, **3,** 326; Dingl. Poly. 1849, **111,** 436; Poly. Centr. 1849, **15,** 686; Jahr. Chem. 1849, **2,** 471.

[6] Compt. rend. 1846, **23,** 1085. Mechanic. Mag. 1847, No. 1239; Dingl. Poly. 1847, **105,** 156.

deduced that, representing cellulose according to Payen as $C_{12}H_{10}O_{10}$, the nitrocotton "loses one equivalent of water and three equivalents of nitric acid." T. Ransome,[1] J. Gladstone,[2] Fehling,[3] P. van Kerckhoff and F. Reuter,[4] E. Hecker and E. Schmidt,[5] M. Pettenkofer[6] and J. Pelouze,[7] independently, analyzed guncotton, but from their analyses formulas were adduced of wide variance.

P. van Kerckhoff reported[8] that guncotton is profoundly modified upon heating to 150°, explodes at 132° when rapidly heated, but when heated slowly passes 180° 200° without deflagration. R. Porret[9] and with E. Teschemacher,[10] heated slowly from 38° to 67°, guncotton dissolved in nitric acid, obtaining a limpid liquid without gas evolution, from which the guncotton was precipitated in a powdery form without change in properties. P. Weiss[1] endeavored to determine by calculation the effect of guncotton in relation to ordinary powder, but "as the author's statements are based upon the somewhat inaccurate analysis of Fehling, we refrain from following him into the details of his speculations."

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[1] Phil Mag 1847, (3), **30**, 1, Jahr Chem 1847 1848, **1**, 1132 Liebig, Kopp's Ann Rep 1847–1848, **2**, 366 C Marr, J Chim med May, 1850, Chem Gaz. 1850, No 175, Dingl Poly 1850, **116**, 450, 472 G Marr, Dingl Poly 1857, **145**, 73

[2] Mem Chem Soc 1848, **3**, 412, Pharm. J Trans **11**, 401, **13**, 215; Phil Mag. 1847, (3), **31**, 519, Jahr Chem 1847–1848, **1**, 1139, Jahr Chem. 1853, **6**, 550. Berz Jahr 1848, **27**, 417, 1849, **28**, 353 Reinsch, Jahr Pharm 1849, **18**, 102, Rep Pharm 1849, (3), **3**, 6, Pharm Centr 1849, 506, Jahr Chem 1849, 469; Berz Jahr 1851, **30**, 371, Arch Pharm **18**, 271, J prakt Pharm 1849, **47**, 477, Poly Centr 1849, **15**, 467, Dingl Poly 1849, **114**, 432

[3] Dingl Poly. 1847, **103**, 220, 224, Liebig and Kopp's Ann. Report, 1847 1848, **2**, 366, Jahr. Chem 1847–1848, **1**, 1132

[4] J. prakt Chem 1847, **40**, 262–284; Compt rend 1846, **23**, 114, 1847, **24**, 46, abst. Liebig, Kopp's Ann Rep 1847–1848, **2**, 363, 370, 371, Berz Jahr. 1849, **28**, 346, Jahr Chem 1847–1848, **1**, 1129, 1137. Compare J prakt. Chem. 1847, **40**, 193, 1848, **43**, 242, Ann 1847, **64**, 391.

[5] J. prakt Chem 1847, **40**, 257, Poly Centr. 1847, **13**, 36, Liebig and Kopp's Ann Report, 1847–1848, **2**, 364, 373, 374, Jahr. Chem. 1847–1848, **1**, 1130, 1141

[6] Dingl. Poly. 1846, **102**, 445, Bayer Kunst. Gewer. 1846, 57 Compt. rend 1846, No 18, 19, 21, Dingl Poly 1847, **103**, 42, 48 Bayer Kunst Gew Blatt. Jan 1847; Dingl Poly 1847, **103**, 209, 219.

[7] Compt rend 1847, **24**, 2, Dingl. Poly 1847, **103**, 224; Pogg Ann 1847, **71**, 144 Wag Jahr. 1864, **10**, 237. See also Anthenaeum, No 996; abst Amer. J. Sci 1847, **3**, 142, 259.

[8] J prakt Chem 1847, **40**, 284 287, 1848, **43**, 242, abst Berz Jahr 1847, **28**, 350, 353; Jahr Chem. 1847–1848, **1**, 1137; Liebig, Kopp's Ann. Rep. 1847–1848, **2**, 370; Compt. rend 1846, **23**, 1140; Annuaire Chimie, 1847, **3**, 454. Pharm. Centr 1847, 690. Ann. 1847, **64**, 391. See also J. prakt. Chem 1847, **40**, 193; **43**, 242.

[9] Phil. Mag. 1847, (3), **30**, 409, Chem Soc Mem. 1848, **3**, 287, J. prakt. Chem 1847, **41**, 208; Chem. Centr. 1847, **18**, 689, Jahr Chem 1847–1848, **1**, 1138. See Teschemacher, Phil. Mag 1847, (3), **30**, 258; Liebig, Kopp's Ann. Rep. 1847–1848, **2**, 370; Mem Chem Soc 1848, **3**, 253.

[10] Phil. Mag. 1847, **30**, 273; Mem Chem Soc. 1848, **3**, 258; Jahr. Chem. 1847–1848, **1**, 1141. Chem. Gaz. No 101, 28; abst. Berz Jahr. 1848, **27**, 422, 423. Kalindt, Pogg. Ann. 1847, **70**, 168; Berz. Jahr. 1849, **28**, 351; Jahr. Chem. 1847–1848, 1137; Dingl. Poly. 1847, **103**, 214.

Wartmann,[2] Talbot,[3] Schröder,[4] B. Silliman,[5] Mosander,[6] R. Oxland,[7] Kindt,[8] Berthault,[9] Bacon,[10] Coathupe,[11] T. Adams,[12] C. Despretz,[13] contributed desultory results to this subject in 1847. W. Reid[14] refers to a German botanist, Hartig, as the discoverer of nitrocellulose, he (Hartig) having in 1847 dissolved guncotton and used the product as a propellant.

F. Domonte and Menard determined the solubility of nitrocellulose in ether,[15] Richier in methyl and ethyl acetates,[16] while

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[1] Dingl. Poly 1847, **103,** 370, Liebig and Kopp's Ann Rept. 1847–1848, **2,** 375; Jahr. Chem. 1847 1848, **1,** 1143 Pharm Ztg. 1891, 113, Wag. Jahr 1891, **37,** 749.

[2] Arch. ph. nat **4,** 193, Jahr Chem 1847- 1848, **1,** 1144, Liebig, Kopp's Ann. Rept. 1847- 1848, **2,** 376.

[3] Dingl. Poly. 1847, **105,** 245, Rept Pat Inv, July 24, 1847.

[4] Mannheimer Gewerbe. Blatt. 1847, No. 12 and 13, Dingl. Poly. 1847, **105,** 74; 1848, **108,** 465.

[5] Amer. J. Sci. 1847, (2), **3,** 102

[6] Oefvers. af K. Vet. Foerhandl III, 290, Berz Jahr. 1847, **27,** 416

[7] Chem. Gaz. 1847, 340, Dingl. Poly. 1847, **106,** 76, Liebig and Kopp's Ann Rept. 1847–1848, **2,** 375.

[8] Pogg. Ann. 1847, **70,** 167; Dingl. Poly 1847, **103,** 214; Liebig and Kopp's Ann Rept 1847–1848, **2,** 370. Berz Jahr 1849, **28,** 351; Jahr Chem 1847–1848, **1,** 1137.

[9] Compt rend 1847, **24,** 566.

[10] Amer J. Sci. 1847, (2), **4,** 445, Proc Boston Soc. Nat Hist. 1847, 195.

[11] Phil. Mag 1847, (3), **31,** 152; Liebig and Kopp's Ann Rept 1847–1848, **2,** 374, Jahr. Chem 1847- 1848, **1,** 1142

[12] Amer J. Sci. 1847, (2), **4,** 139.

[13] Compt. rend. 1846, **23,** 678

[14] W. Reid says (J S. C. I 1911, **30,** 851; abst C A 1911, **5,** 3341): "I was not the first, however, to dissolve nitrocellulose and utilize the product for propulsive purposes Fifteen years before, the process had been worked out, I learnt that a German botanist, Hartig, had made experiments in this direction in 1847 The pamphlet to which he refers in his experiments is exceedingly rare; I know of only one copy in Great Britain, and I have been unable to obtain it in Germany, therefore my ignorance on the subject in 1881, may, perhaps be excusable"

[15] Compt. rend. 1846, **23,** 1087; 1847, **24,** 89, 390; Amer. J. Sci. 1847, (2), **4,** 140; Phil. Mag. 1847, **31,** 519; Berz. Jahr. 1849, **28,** 348; Jahr. Chem. 1847–1848, **1,** 1136; Rec. Trav. 1847, 104; J. Pharm. 1847, (3), **12,** 159; Pogg. Ann. 1847, **71,** 144; Liebig and Kopp's Ann. Report, 1847–1848, **2,** 367; Chem. Centr. 1847, **18,** 892; Ann Rep. Chem 1847–1848, 377; Annuaire de Chimie, 1847, 454.

[16] Compt. rend. 1847, **24,** 392, Berz. Jahr. 1849, **28,** 348; Jahr. Chem.

Sourisseau,[1] Lepage[2] and C. Grüel[3] critically examined the properties of nitrocellulose ether-alcohol solutions.

Morin[4] cited many erratic instances of the propulsive power of guncotton, in which, by too rapid combustion, firearms had been burst. W. Crum[5] proceeded in a circumspect and careful manner in nitration experiments, commencing with the preliminary preparation of raw cotton. He employed fine Sea Island fiber, which was carded, bleached, boiled in caustic soda, and finally digested with dilute nitric acid. After each operation, the cotton was placed in a filter bag and exhaustively washed. When thus purified it had lost 5.6% in weight and contained but 0.09% ash. In order to convert the cotton into nitrate it was dried and introduced in little parcels of 10 grains each, while still warm, into one ounce of acid mixture, consisting of sulfuric acid (1.84 sp. gr.) and nitric acid (sp. gr. 1.517) in the ratio of one to three by volume. The nitrocotton contained 0.22% ash, and appears to have been unusually stable.

Pelouze in 1846 (see p. 1569) made an exhaustive series of careful experiments on the production and ballistic properties of guncotton, and clearly set forth that the properties are radically influenced by impurities and extraneous matter. Just as in gunpowder, the density, and shape and size of the granules alters their properties, Pelouze demonstrated the period of nitration, and the degree of initial purification of the cotton, influenced markedly the uniformity and stability of the nitrocotton.

Kamarsch and Heeren,[6] as well as A. Knop,[7] allowed the

1847–1848, **1**, 1139; J. Pharm (3), **14**, 263, J. Chim. Med. (3), **4**, 541; J prakt Chem. 1848, **44**, 376; Liebig & Kopp's Ann. Rept. 1847–1848, **2**, 372.

[1] N. J. Pharm. 1848, **14**, 417; Dingl. Poly. 1849, **111**, 431. Liebig, Kopp's Ann. Rept. 1847-1848, **2**, 372, 373.

[2] J. pharm. (3), **14**, 420; abst. Liebig, Kopp's Ann. Rept. 1847–1848, **2**, 372, 373 See Nickles, J Pharm. (3), **39**, 158, Jahr. Chem. 1860, **13**, 499.

[3] Pogg. Ann. 1848, **75**, 333; Dingl. Poly. 1848, **110**, 412; Liebig Kopp's Ann. Rept. 1847–1848, **2**, 372, 373.

[4] Dingl. Poly. 1849, **111**, 429; Poly. Centr. 1849, **15**, 690; Berz. Jahr. 1849, **28**, 350; 1851, **30**, 367; Compt. rend. 1849, **28**, 105, 144, 146; Liebig, and Kopp's Rept. 1849, **3**, 326; J. de Pharm. 1848, 417. Piobert and Morin, Compt. rend. 1846, **23**, 811, 903, 1001; Annuaire de Chimie, 1847, **3**, 454. For biography of Piobert, giving also a list and abstracts of his work on guncotton and explosives, see Rev. Sci. 1871, **8**, 434.

[5] Phil. Mag. 1847, (3), **30**, 426; abst. J. prakt. Chem. 1847, **41**, 201; J. Pharm. 1847, (3), **12**, 296; Jahr. Chem. 1847–1848, **1**, 1130; Glasgow Phil. Soc. Proc. 1844–1848, **2**, 163; Ann. 1847, **62**, 233.

[6] Dingl. Poly. 1846, **102**, 165.

[7] Chem. Centr. 1849, **21**, 801; 1850, 49; Ann. 1850, **74**, 347; J. prakt.

cotton to remain for several minutes in a mixture of 2 parts by weight of sulfuric acid and one part of fuming nitric acid, Knop using a mixture of equal volumes of both. P. v. Kerkhoff and Reuter employed one part of cotton to 48 parts of a mixture of equal parts by weight of strong nitric and sulfuric acids, the yield being 176% on the cotton. All of the above investigations were communicated in the years 1846 and 1847, and are indicative of the tremendous interest which this subject aroused.

Guncotton Investigations 1848-1850. The writings during this period of C. Grüel,[1] F. Zantedeschi,[2] M. Loam,[3] D. Philipp,[4] Reindl,[5] R. Rikli,[6] Wenedickt,[7] Westerling and Staaf,[8] Wrede,[9] Berzelius,[10] Combes,[11] are comparatively of minor interest. A. Seguier[12] showed by carefully constructed graphs of the range of sportsmen's black powder and guncotton, that the ballistics of the latter were incontestably superior for equal weights. A. Payen,[13] Cavilli,[14] E. Souberian[15] and Sourisseau,[16] corroborated

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Chem 1849, **48,** 362, 1852, **49,** 228; Jahr Chem. 1849, 466, Chem. Gaz, 1850, 81; Compt. rend 1846, **23,** 808. Dingl. Poly 1846. **102,** 165. A. and W. Knop, J. prakt Chem. 1849, **48,** 362, 1852, **56,** 334; Chem. Gaz 1850, 81, Ann 1850, **74,** 347, Chem Centr. 1852, **23,** 129, 423; Jahr Chem 1852, **5,** 657

[1] Pogg. Ann. 1848, No 10, 14, **75,** 333; Dingl Poly 1848, **110,** 412 Liebig, Kopp's Ann Rept 1847-1848, **2,** 372, 373

[2] Oefvers. af K Acad. Foerhandl. **4,** 5; abst Berz. Jahr Chem. 1848, **27,** 418.

[3] E P 12405, 1849; abst Dingl Poly 1849, **114,** 106; Rept Pat Inv. 1849, 77

[4] Poly. Centr 1848, **14,** 1533. Berliner. Gew Ind u Handelsblatt. **29,** 151, Dingl Poly 1849, **111,** 232, Chem Tech Mitth. 1848-1850, 17.

[5] Poly. Centr. 1848, **14,** 1533

[6] J. prakt. Chem. 1849, **46,** 191; abst Berz Jahr. 1851, **30,** 368; Dingl. poly. 1849, **111,** 467.

[7] Wenedickt, "Erfindung, hochstwichtige, Die Schiessbaumwolle eine anwessung zur Bereitung derselven," 8. Wem, 1846

[8] Oefvers. af K. Acad Forhandl. **3,** 320; abst. Berz Jahr. 1848, **27,** 416.

[9] Oefvers. af. K. Acad. Forhandl. **3,** 291; abst. Berz. Jahr. 1848, **27,** 416.

[10] Berz Jahr. Chem. 1848, **27,** 410, 413. Ofvers. af Vet Acad. Forhandl **3,** 233, 283.

[11] Compt rend. 1846, **26,** 61; Amer J. Sci. 1848, (2), **6,** 256; Dingl. Poly. 1848, **108,** 141; Liebig and Kopp's Annual Report, 1847-1848, **2,** 376; Jahr Chem. 1847-1848, **1,** 1144.

[12] Compt. rend 1846, **23,** 862, 959, 1047. Annuaire de Chimie, 1847, **3,** 454; Majocchi Ann. Fis. Chim. 1847, **25,** 116. Rev. Scient. **28,** 90; Berz. Jahr. 1849, **28,** 350.

[13] Compt. rend. 1846, **23,** 905; N. Ann. Sci. Nat. Bot. **10,** 161; Annuaire de Chimie, 1847, **3,** 454. Compt. rend. 1846, **23,** 999; Berz. Jahr. 1849, **28,** 348, 350; Annuair de Chimie, 1847, **3,** 454. Compt. rend. 1846, **23,** 1088; Annuaire de Chimie, 1847, **3,** 454. Compt. rend. 1846, **23,** 1096; Berz. Jahr. 1848, **29,** 350; Annuaire de Chimie, 1847, **3,** 454. Compt. rend. 1847, **24,** 85; Jahr. Chem. 1847-1848, **1,** 1139; Annuaire de Chimie, 1847, **3,** 454. Compt. rend. 1864, **59,** 415; Dingl. Poly. 1864, **174,** 385; Poly.

these results. C. Mann,[1] first brought out the facts that the percentage of water in the nitric-sulfuric acid mixture influences greatly not only the yield, but the solubility of the product as well, and laid down definite rules for the formation of nitrocotton of maximum solubility in named solvents and solvent combinations.

C. Marx[2] carried out careful experiments of the temperature of inflammation of guncotton, and determined that guncotton "prepared in the ordinary manner" may explode from 63° up to 91° and above, depending upon the speed with which the temperature was raised in making the determination. About this time Maurey,[3] "who had been engaged in the manufacture of guncotton on a large scale," published the fact that whereas a kilo of guncotton cannot be prepared for less than 7 francs, and the same amount of blasting gunpowder costs 1.17 fr. and fine gunpowder 2.39 fr., to produce an equal effect for the same price, guncotton must exert six times the effect of the former and three times the effect of the latter. Three gm. of guncotton, however, produces the effect of only 5 gm. of extra fine gunpowder. Maurey observed that decomposition of guncotton was hastened by the presence of small traces of sulfuric acid in it, "since this acid is never completely removed by washing with water," and that when washed with alkaline water, explosion was prone to occur, as his practical experience could attest.

Along the lines of attempting to utilize nitrocotton in solution,

Centr 1865, **31,** 196· Jahr Chem 1864, **17,** 570, Wag. Jahr 1864, **10,** 245. Bull Soc d'Encour. 1868, 714, Dingl Poly 1869, **192,** 67

[14] Oefvers. af K. Vet Acad Foerhandl **3,** 321, abst Berz. Jahr. Chem. 1848, **27,** 418.

[15] N. J. Pharm. 1848, **14,** 263, Dingl Poly. 1848, **110,** 414; Chem. Tech. Mitth. 1848–1850, 17.

[16] N. J Pharm. 1848, **14,** 417, Dingl Poly 1849, **111,** 434 Jahr Chem. 1847–1848, **1,** 1139.

[1] Compt. rend. 1850, **30,** 667, Poly. Centr. 1850, **16,** 1020; Dingl. Poly. 1850, **116,** 473. Petersb. Acad Bull. 1853, **11,** 209, Ann 1853, **88,** 351; Pharm. J. Trans. 1853, **13,** 68; J Pharm. 1853, (3), **24,** 371; Poly. Centr. 1853, **19,** 1002; Chem. Centr. 1853, **24,** 393, Dingl Poly 1853, **129,** 114; J. prakt. Chem. 1853, **59,** 241; Amer. J. Pharm. 1853, **25,** 529, Jahr. Chem. 1853, **6,** 547.

[2] Pogg. Ann. 1849, **78,** 100, 360; Jahr. Chem. 1849, **3,** 325; Berz. Jahr. 1851, **30,** 368; Poly Centr. 1849, **15,** 1165. Dingl Poly. 1857, **145,** 73, Poly. Centr. 1857, **23,** 1179

[3] Compt. rend. 1849, **28,** 343; Liebig and Kopp's Ann Rep. 1849, **3,** 325; Poly. Centr. 1849, **15,** 688; Dingl. Poly. 1849, **112,** 138; Berz. Jahr. 1851, **30,** 366; Jahr. Chem. 1849, **2,** 471.

are the collodion experiments of E. Parrish,[1] J. Leidy,[2] J. Lassaigne,[3] J. Edwards,[4] F. Dumonte and Menard[5] and H. Vohl.[6] Their work was more along pharmaceutical lines, in endeavors to extend the usefulness of nitrocotton as a protective covering, and as a component of antiseptic dressings. The publications of Svanberg,[7] A. Strecker,[8] and the work of v. Frankenstein[9] were more in the nature of a critical digestion of work already disclosed.

Guncotton Development, 1851 to 1860. In the biennial period 1851–1852 appeared the investigations of F. Heeren,[10] Krell,[11] J. Bingham[12] and G. Winkelblech,[13] disclosing nothing radically new. O. Livonius[14] distinguished by methods of preparation, how ether-soluble and ether-insoluble cellulose nitrates might be prepared, and described a method of formation on a commercial scale of nitrocotton entirely soluble in ethyl acetate. He observed that ethyl acetate solutions of nitrocellulose did not possess the adhesive and agglutinating qualities as the solution in ether. The etheroxylin (*ether*, *pyroxylin*) of J. v. Winiwarter[1] was protected by patent issuance, consisting of pyroxylin 75 in ether 100 parts (an impossibly heavy solution) which was to be used as a nipple for firing gun matches, when combined with mercury fulminate, $KClO_3$ and charcoal.

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[1] Amer. J. Pharm. 1849, **21,** 289. See E. Parrish and W. Livermore, Amer. J. Pharm. **14,** 181.

[2] Amer. J. Pharm. 1850, **22,** 24.

[3] J. Chim. Med. 1848, 541; Dingl. Poly. 1848, **110,** 65, Chem. Tech. Mitth. 1848–1850, 16

[4] Amer. J. Pharm 1849, **21,** 233; Jahr Chem. 1849, **3,** 27; J. Chim. Med. (3), **5,** 511; Dingl. Poly. 1849, **114,** 157; Jahr Chem. 1849, **2,** 473 Brit Assoc Rep 1854, II, 66 Liverpool Lit Phil. Soc. Proc. 1854–1855, **9,** 16

[5] Rec des Trav de la Soc. d'Emul. J. les Sci. Pharm 1847, 104; Amer. J. Sci. 1848, (2), **5,** 265

[6] Ann. 1849, **70,** 360, Poly. Centr. 1849, **15,** 1464, Amer. J. Sci. 1849, (2), **8,** 117; Lond. J. and Repert, **34,** 280, Technologist, Liebig and Kopp's Ann. Rept. 1849, **3,** 326; Jahr. Chem. 1849, 472; Berz. Jahr. Chem. 1851, **30,** 368. Ann. 1856, **99,** 125; J. prakt. Chem. 1856, **69,** 299; Ann. Chim. Phys. 1856, (3), **48,** 380; Arch. ph. Nat. **33,** 153; Jahr. Chem. 1856, 669. Ann. 1858, **105,** 330; J. prakt Chem. 1858, **75,** 125; Chem. Centr. 1858, **29,** 446; Jahr. Chem. 1858, **11,** 489.

[7] Oefvers. af K. Vet. Acad. Foerhandl. **3,** 322; **4,** 51, 52 Berz. Jahr. 1848, **27,** 389, 417; 1849, **28,** 353; Chem. Centr. 1848, **19,** 702. See Svanberg and Staaf, Œfvers. af. K. Vet. Acad. Foerhandl **4,** 171; **5,** 4; Berz. Jahr. 1849, **28,** 360, 361; Jahr. Chem. 1849, **2,** 166; 1856, **9,** 662. Wag. Jahr. 1861, **7,** 234.

[8] Ann. 1848, **69,** 111; 1850, **73,** 59; **74,** 347; Chem Centr. 1850, **21,** 49; Ann. rep. Chem. 1849, **3,** 323; Chem Gaz. 1850, 149; Jahr Chem. 1856, **9,** 662.

[9] Die Schiessbaumwolle; Ihre chem. physis. Eigenschaften und Wirkung. Nebst. Anleitung zur Erzeugung der Schiessbaumwolle, etc., mit Holzschn. 16: Graz. 1846. (Leipzig, G. Wigand.)

[10] Mitt. Hannover Gewer. 1852, 64, 65; 1856, 158; Dingl. Poly. 1852, **125,** 208; 1856, **141,** 279; 1866, **180,** 406.

[11] Reichke's Wochenblatt, 1852, No. 7; Dingl. Poly. 1852, **123,** 455. Technologiste, 1852, 249; Dingl. Poly. 1852, **124,** 64.

[12] Compt. rend. 1852, **34,** 725; Dingl. Poly. 1852, **125,** 28; Ann. 1852, **84,** 173; Jahr. Chem. 1852, **5,** 216; J. prakt. Chem. 1852, **56,** 485.

[13] J. Pharm. 1850, 428; Dingl. Poly. 1851, **119,** 318.

[14] Archiv. d. Pharm **18,** 271; Berz. Jahr. 1851, **30,** 369; J. Pharm. et Chim. 1849, (3), **15,** 468; **16,** 122.

During 1853–1854 appeared the first contribution to this art by A. Bechamp,[2] followed by Hamolatsch,[3] Hirzel,[4] T. Woods,[5] E. Hadow[6] and Bredschneider.[7] Bechamp by the action of reducing agents on guncotton, came to the conclusion that the latter was an ester of cellulose, and this important observation has since repeatedly been verified. Furthermore, he engaged himself with the problem of determining the number of distinct nitrocelluloses which are capable of existence (see p. 1650) and admitted the existence of three definite compounds. These two generalizations had a far-reaching significance. It was the beginning of the establishment of this art from a chaotic empiricism, to a well defined and logical basis, and undoubtedly paved the way for the more exact measurements and generalizations which were so soon to follow. The P. Berard[1] patents for commercial employment of collodion as varnish and lacquer were issued;[1] J. Spiller and W. Crookes[2] disclosed useful information on the preparation of nitrocelluloses especially suitable for distinct purposes, while J. Gladstone[3] published his accumulated experience of four years' observation of the gradual decomposition of guncotton. He made careful analyses in attempts to classify the nitrated celluloses according to the nitrogen content (see p. 1643), but his analytical results have been called in question by subsequent workers. In conjunction with J. Russel,[4] a report of the guncotton as introduced by the Austrian Government for filling hollow projectiles was made—being an exhaustive epitome of the existing information up to that time.

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[1] E P. 13935, 1852, E P 306, 1853; abst Mechan Mag **57,** 135, 219.

[2] Compt. rend. 1852, **35,** 473, Dingl Poly 1852, **126,** 114, Instit. 1852, 318; Pharm. Centr 1852, 823; Jahr Chem 1852, **5,** 658; J prakt. Chem 1853, **58,** 15, Ann Chim Phys. 1853, **37,** 207. Chem Gaz , Nov. 15, 1852; Amer. J Pharm 1853, **25,** 159; N J Pharm 1852, **22,** 440. Chem. Tech. Mitth. 1852–1854, 164 Compt rend 1853, **37,** 134, Instit 1853, 261; J. prakt. Chem 1853, **60,** 187, Pharm. Centr. 1853, 703; Poly Centr. 1853, **19,** 687; Jahr Chem. 1853, **6,** 550, Amer. J Sci. 1853, (2), **16,** 406, Ann Chim. Phys. 1856, **46,** 338. Compt rend. 1855, **41,** 817; Ann. Chim. Phys. 1856, **46,** 338, J prakt Chem 1856, **68,** 51, Jahr. Chem. 1855, **8,** 681 Compt. rend. 1856, **42,** 1213, Inst 1856, 235; Jahr Chem 1856, **9,** 674, Ann. 1856, **100,** 367; J. prakt. Chem. 1856, **69,** 449 Compt rend. 1860, **51,** 257; Zts. Chem. Pharm **3,** 657. Ann Chim Phys 1862, (3), **64,** 311, 322; Chem. Centr. 1862, **33,** 865; 1863, **34,** 690; Wag. Jahr 1862, **8,** 280; Jahr Chem. 1862, **15,** 469; 1863, **16,** 568, Rep. Chim Pure, 1862, **4,** 358; Bull Soc. Chim. 1863, **5,** 289; Ann. Chim. Phys 1855, **44,** 311, 1856, **48,** 458.

[3] Phot. Jahr **18,** 77.

[4] Techn Zts. 1856, **2,** 213.

[5] Bibl. Univ. Suppl. **26,** 357; Dingl. Poly 1854, **134,** 126. See Phil. Mag. 1854, 213.

[6] Poly. Centr. 1853, **19,** 1471; Quart J. C. S 1854, **7,** 201; J. prakt. Chem. 1855, **64,** 169; Chem. Centr. 1855, **26,** 202; Dingl. Poly. 1855, **136,** 397; Amer. Drug. Circ. **8,** 123; Jahr. Chem. 1854, **7,** 626.

[7] Arch. Pharm. **134,** 274; abst. Poly. Centr 1856, **22,** 383.

In 1855 were issued the patented processes of F. Joyce,[5] J. Norton[6] and F. Prince[7] for the employment of guncotton as a protective covering for percussion caps, and the preparation of cartridges. Delahaye,[8] Cutting,[9] L. v. Babo,[10] F. Leblanc[11] and Mansell,[12] made minor observations. In this year appeared the solid collodion of G. Lloyd,[13] of "extraordinary stability." Low disclosed details for the employment of collodion in the grafting of plants and trees.[14]

The next year appeared the work of E. Robiquet and J.

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[1] E. P. 639, 1858; abst. Poly Centr. 1858, **24,** 892, Rept Pat Inv 1858, 131, 134; 1859, **25,** 413, Poly Centr. 1854, **24,** 675; 1859, **25,** 413, Civil Engineer, 1853, 16

[2] Phil. Mag. 1854, 349, Dingl Poly. 1854, **132,** 360, Chem Tech. Mitth. 1852-1854, 33 See also J Spiller, Chem. News, 1865, **12,** 296; abst Bull. Soc. Chim. 1866, **5,** 227, Chem. Centr. 1866, **37,** 45, Jahr. Chem. 1865, **18,** 596.

[3] Mem. Chem Soc. 1848, **3,** 412; Pharm J Trans **11,** 401, **13,** 215; Phil. Mag. 1847, (3), **31,** 519; Jahr Chem. 1847 1848, **1,** 1139; Berz Jahr 1848, **27,** 417; 1849, **28,** 353 Pharm. J Trans **11,** 401, Jahr. Chem. 1853, **6,** 660. Pharm J. Trans **13,** 25; Jahr. Chem. 1853, **6,** 550

[4] Chem News, 1863, **8,** 141; Jahr. Chem. 1863, **16,** 744; Bull. Soc. Chim. 1865, **3,** 468.

[5] E. P. 749, 1855.

[6] E. P. 400, 1855.

[7] E. P. 173, 1855

[8] Bull. Soc. Franç Phot. 1855, **1,** 165, 205.

[9] Bull. Soc. Franc. Phot. 1855, **1,** 210

[10] D. R. P. 8727, 1879; abst. Dingl. Poly. 1880, **236,** 173; J. A C S. 1880, **2,** 103. Wag. Jahr 1855, **1,** 142

[11] Ann. d. pont. 1848, (2), **15,** 13, 113. See Dessaignes, Compt. rend. 1851, **33,** 462; Instit 1851, 347; Ann. 1852, **81,** 251; J. prakt. Chem. 1852, **55,** 33; Jahr. Chem. 1851, 552.

[12] Cosmos, **6,** 265; abst. Poly. Centr. 1855, **21,** 630.

[13] Cosmos, **5,** 600; abst. Poly. Centr. 1855, **21,** 176.

[14] Dingl. Poly. 1855, **135,** No. 10; abst. Mon. Sci. 1857–1858, 848.

Dubosq,[1] J. Spiller,[2] A. Caldwell,[3] and L. Hofmann.[4] The latter increased the suppleness of collodion by the addition of small amounts of castor oil. F. Kuhlmann[5] attempted to differentiate between nitrocellulose, partly nitrated cellulose and decomposed nitrocellulose by the selective action of dyestuffs thereon.

In 1857 should be chronicled the paper of A. Hardwich on the preparation of pyroxylin,[6] and the observations of W. Proctor on methods of formation of Pharmacopeial collodions.[7] C. Bousfield patented for a foreign client,[8] as a primer, a detonating composition of mercury fulminate and collodion. The next year appeared the observations of H. Corbin,[9] P. Gaillard,[10] and G. de Rumine,[11] and the comprehensive article of C. Caspari[12] on collodion of the Pharmacopeia. O. Sherman in an inaugural address to the Philadelphia College of Pharmacy,[13] gave temperatures and composition of acid baths most suitable for the preparation of nitrocelluloses of ether-alcohol solubility.

In 1859 appeared the investigations of X. Landerer,[14] F. Elliot[15] and Nelson,[16] and the collodion cartridge of J. Macintosh,[17]

[1] Compt rend 1856, **43**, 1191, Dingl Poly. 1856, **143**, 189; abst. Poly Centr 1, 1857, 168; Jahr Chem 1856, **9**, 191.

[2] Sc Rev **1**, 180 Phot Archives, 1865, 440; Chem Centr. 1866, **37**, 45, Bull Soc Franc Phot 1867, **13**, 161 R Munsen and L Schischkoff; Ann Phys Chem 1857, No 11, Dingl Poly 1858, **147**, 413.

[3] Edinb new Phil J **5**, 380, Wag Jahr 1857, **3**, 357. Jahr. Chem. 1859, **12**, 543; J Pharm (3), **37**, 240 Compt rend 1859, **48**, 202; J. Pharm. 1859, **35**, 81, Rep Chim Pure, **1**, 269, Mon Sci 1859-1860, **2**, 894.

[4] Chem Gaz Oct 15, 1856, Archiv Pharm **137**, 146, Amer J. Pharm 1857, **29**, 64, Dingl Poly 1856, **141**, 399, Poly Centr. 1856, **27**, 1470, Chem Tech Mitth 1856–1857, 18

[5] Compt rend 1856, **42**, 673, 711, J prakt Chem. 1856, **69**, 288, 293, Dingl Poly 1856, **142**, 221, 1857, **140**, 223, Poly Centr 1856, **22**, 658, 870, Wag Jahr 1856, **2**, 327, 329

[6] Bull Soc Franc Phot 1857, **3**, 343, 1858, **4**, 264, 1860, **6**, 14, 98. Poly Centr. 1866, **32**, 75. Rep Chim Appl 1860, **2**, 65; Jahr Chem 1860, **13**, 499

[7] Amer J Pharm 1857, **29**, 106, 1864, **36**, 304

[8] E. P. 2882, 1857.

[9] Bull Soc. Franc Phot 1858, **4**, 62

[10] Bull. Soc Franc. Phot. 1858, **4**, 331.

[11] Bull Soc. Franc Phot 1858, **4**, 174

[12] J and Trans. Maryland, Co l Pharm, June, 1858; Amer. J. Pharm. 1858, **30**, 371.

[13] Am J Pharm 1858, **30**, 212

[14] Wittstein Vierteljahr. prakt Pharm. **8**, 201; Dingl. Poly. 1859, **151**, 468, Chem. Tech Mitth 1858–1859, 27, Poly. Centr. 1859, **25**, 1697.

[15] Bull. Soc Franc. Phot. 1859, **5**, 110 In this connection, see A. Elliot, J. A. C. S. 1882, **4**, 147, 186; Proc. U S. Nav. Inst. 1882, **8**, 449.

[16] Bull. Soc. Franc. Phot 1859, **5**, 313

[17] E. P. 2791, 1859; 1295, 1860.

formed by dipping a mandrel into a solution of guncotton. The following year saw the issuance of the J. Lemoine patent[1] for nitrocellulose manufacture, the nitro-parchment of V. Kletinsky,[2] the guncotton formation process of E. Matthew-Plessy,[3] and the contributions of Poitevin,[4] and of Peschard.[5] A. Hofmann[6] determined the presence of oxalic acid among the products of spontaneous decomposition of guncotton. P. Lepage[7] and D. van Monckhoven[8] also contributed to the subject. It was in 1860 that the "white gunpowder" of E. Lannoy & Co., afterwards called Lithofracteur, appeared.[9]

While it cannot be controverted that the investigations, memoirs and observations upon the general subject of nitrocelluloses were many and exhaustive in detail, yet during the decade 1851–1860 the question of the underlying causes of erratic stability was the paramount problem in importance, and but little real basic work had been accomplished towards its satisfactory elucidation. Numerous fatal explosions occurring without apparent cause had already begun to stamp the hall-mark of disapproval upon the use of nitrocellulose not only as a propulsive agent, but in the peaceful arts as well, and in some countries due to Government apathy and lack of public funds for continuing research, interest was decidely on the wane.

While it was universally recognized that guncotton possessed great potentialities, when/if ever prepared of high stability and uniformity in composition and properties, the (then fanciful) prediction of Schönbein that it would eventually supplant gunpowder as a fire-arm propellant, seemed almost hopeless of realization. Such, at least was the state of public opinion, at the commencement of the sixties of the century just past. The frequent and disastrous explosions of guncotton that shook the countryside had shaken the confidence of the people as well.

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[1] F. P. 26629, 47522, both of Nov. 23, 1860

[2] Dingl. Poly. 1860, **156,** 385; Stamm's Illust Wochenschrift, May 1860, No. 19. Dingl. Poly. 1860, **156,** 463, Phot Archiv 1860, 103.

[3] F. P. 46470, 1860.

[4] Bull. Soc. Franc. Phot. 1860, **6,** 115.

[5] Bull. Soc. Franc. Phot. 1860, **6,** 161.

[6] Ann. 1860, **115,** 281; Dingl. Poly. 1860, **158,** 237; Wag. Jahr 1860, **6,** 466; Chem. Centr. 1860, **31,** 976; Poly. Centr. 1860, **26,** 1483; Jahr Chem. 1860, **13,** 499; Rep. Chim. Applique. 1861, **3,** 119; J. C S. 1860, **13,** 76. Ber. 1879, **12,** 1126. R. Wagner, J. prakt. Chem. 1854, **61,** 125. Dingl. Poly. 1872, **205,** 75; Deut. Ind. Ztg. 1872, No. 17.

[7] See J. Nickles, J. Pharm. 1861, **39,** 158; Jahr. Chem 1860, **13,** 499. See also J. Pharm. Chim. (3), **14,** 420. Leguier and Clerget, Compt. rend. 1864, **23,** 862. A. Loir, Bull. Soc. Chim. 1861, **12,** 113; Jahr. Chem. 1861, 729; Amer. Pharm. Assoc. 1863, **11,** 145. F. Lucius, Dingl. Poly. 1862, **166,** 63; Chem. Centr. 1862, 925.

[8] Rept. de Chim. Appl. 1860, **2,** 2; Wag. Jahr. 1860, **6,** 466. Wieck's Gewerbeztg. 1863, 367; Bull. Soc. Franc. Phot. 1863, **9,** 145; 1872, **18,** 8, 22; Dingl. Poly. 1872, **203,** 323, 324; J. C. S. 1872, **25,** 532; Photo. Mitth. 1871, 226; Mech. Mag. 1872, 47.

[9] Berggeist, 1859, No. 84; Poly. Centr. 1860, 343; Wag. Jahr. 1860, **6,** 207.

Stability of Guncotton, and Baron von Lenk. From 1861 onwards, the energies of investigators in this field were focussed on the question of improvement in stability. Among the foremost minds of this period the idea had percolated in and gained firm anchorage that if the stability of this product was not made satisfactory the day was not far distant when guncotton would be a chemical curiosity, mentioned in the text-books but not found in the trade.

M. Bonet made some useful observations on the spontaneous decomposition of nitrocotton, and determined its acceleration in light.[1] M. Chevreul communicated[2] that he had kept guncotton bottled in the dark for over ten years and it remained perfectly stable, but afterwards in exhibiting the sample to some friends, the stopper blew out. Rutzki,[3] A. Martin,[4] A. Müller,[5] added their quota towards making the subject more transparent/opaque. S. de Luca did some really useful work:[6] he examined the products of the combustion of cellulose nitrate, extracting the explosive with water at frequent intervals and making quantitative analyses

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1. Compt. rend 1861, **53,** 405, Chem Centr. 1862, **33,** 512; Jahr. Chem. 1861, **14,** 712; J. prakt. Chem. 1861, **85,** 380; Rep Chim. Pure, **4,** 15; Wag. Jahr. 1861, **7,** 517; Dingl Poly. 1861, **162,** 132, 137; Poly. Centr. 1861, **27,** 1519; Amer. J. Pharm 1862, **34,** 187.

2. Compt. rend 1861, **53,** 407; abst. J. prakt Chem. 1862, **85,** 381. See Jahr. Chem. 1861, **14,** 713. Compt rend. 1864, **59,** 417.

3. Oestr. Milit. Ztschr. 1862, **3,** 1, 63, 149; **4,** 373.

4. Bull. de la Soc. Fran. de Phot. 1861, **7,** 142; Rep. Chim. Pure Appl. **3,** 257, Jahr. Chem. 1861, **14,** 712.

5. Oestr. Milit Zts. 1861, **3,** 245. Reimann's Farber. Ztg. 1871, 298, 325, 348, 363; Dingl. Poly. 1871, **202,** 458, Deut. Ind. Ztg. 1871, 464; Chem. Centr. 1872, **43,** 40.

6. Compt. rend. 1861, **53,** 298, 405; Instit. 1861, 275; Dingl. Poly. 1861, **162,** 135, 137; J. prakt. Chem. 1862, **85,** 378; J. Pharm. 1862, (3), **41,** 483; Chem. Centr. 1861, **32,** 1519; Wag. Jahr. 1861, **7,** 517; Poly. Centr. 1862, **28,** 221; Jahr. Chem. 1861, **14,** 713; Am. J. Pharm. 1862, **34,** 401. Compt. rend. 1864, **59,** 487; Dingl. Poly. 1864, **174,** 388; Poly. Centr. 1865, **31,** 197; Proc. U. S. Nav. Inst. 1864, **10,** 220; Mon. Sci. 1864, 950; Wag. Jahr. 1864, **10,** 243; Amer. Drug. Circ. Feb. 1866; Am. J. Pharm. 1866, **38,** 179.

of the aqueous extract. His manipulative work was clever, but his generalizations faulty.

F. Luchs[1] described his process of guncotton manufacture, "which never permits failure in the satisfactory accomplishment of the task." He "threw in" 18 lbs. of niter to 19 lbs. English sulfuric acid, stirred with a "wooden club," and threw in 2 lbs. of cotton in "lumps about the size of your fist." He removed acid from the nitrated product by alternate washing with water and alcohol. Whether he knew it or not, a step in advance had been made in the removal of some of the lower nitrated esters by this alcoholic treatment. E. Garniere[2]—along photographic lines—added water glass to enhance the stability. So much otherwise valuable time appears to have been lost in futile but heated polemics over priority of conception (not execution) of alleged epoch-making discoveries, that it is difficult, even in the perspective of a half-century elapsed, to obtain a clear-cut and lucid conception of the chronological steps in advancement. A digestion of the multiplicity of contributions which appeared up to this time, however, points clearly to the fact that the psychological moment was fast approaching when the subject in its entirety must either be abandoned or some radical process must be advanced for insuring uniformity and stability, in the manufactured product. At this critical point Baron von Lenk, partially stepped into the breach.

It seems that von Lenk, under the auspices of the Austrian Government, had been more persevering (or foolhardy) than others, and had stuck assiduously to the problem of the manufacture of guncotton in a commercial manner of accepted uniformity in composition and stability. He made a radical departure in having the sense of discernment to appreciate that the state of purity of the initial raw cotton was the first important step in the successful solution of the problem, and he had the personal qualities which backed up his convictions by careful and un-

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1. Dingl. Poly. 1862, **166,** 63; Chem Centr. 1862, **33,** 925, 1233; Jahr. Chem 1862, 467; Wieck's Gwz. 1862, 351; Jahr. Chem. 1862, **15,** 467; Gewerbeblatt aus Wurttemberg, 1863, **13,** 28 Poly. Centr. 1863, **29,** 270; Poly. Notiz, 1864, **19,** 12. H. Hlasiwetz and L. Pfaundler, Ann. **127,** 362; Chem. Centr. 1864, 55.

2. Repert. de Chimi. Appl. III, 337. Wag. Jahr. 1861, **7,** 253; Poly. Centr. 1862, **28**. 1233.

remitting work. His work is of prime importance.

For some years previous to 1862 v. Lenk had been manufacturing, in commercial quantities, nitrocellulose subsequently used as a bursting charge in cannons. It was found, however, that these often burst in the bore, obviously due to the sudden shock of the discharge exploding the shell charge, it having been noted that when gunpowder was used to fire the guncotton shells no ruptures occurred. On July 30, 1862, the magazine at Hirtenberg exploded, and this seems to have finally decided the Austrian governmental authorities to officially abandon guncotton as a desirable propulsive explosive. The veil of secrecy was lifted, and v. Lenk was allowed to communicate his experience to other Powers. Another magazine exploded on Steinfelder Heath near Vienna in 1865, and on October 11th of the same year, the manufacture in Austria was officially abandoned.[1]

In 1862[2] and 1863[3] patents were granted to him in England in the name of J. Revy, and the same year, with official sanction, he came to England and described his methods of guncotton purification to a delegation of the British Association.[1] A factory was erected by Prentice & Co., who started the manufacture of "Baron Lenk's improved guncotton" at Stowmarket, but an explosion occurred there soon after. In the United States the Lenk patent was granted in 1864.[2]

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[1] Wag Jahr 1863, **9,** 310, Schweiz pol z 1864, 30, Poly Centr 1863, **29,** 1171, 1645, 1864, **30,** 1183, Geweblatt aus Wurttemberg, 1863, **13,** 417, Wag. Jahr 1864, **10,** 235, Chem Centr 1864, **35,** 906, Jahr. Chem. 1864, **17,** 796, Sci Amer July 9, 1864, Dingl Poly 1864, **178,** 145 Chem. Tech Mitth 1863, **13,** 64, 159, 1864 1865, 176, Deut. Ind. Ztg. 1864, No 23, Chem News, 1862, **6,** 180 Wag Jahr 1865, **11,** 411; Chem Centr 1865, **36,** 457, Chem Tec Rep 1865, **4,** II, 117; Poly. Centr. 1865, **31,** 1644, Deut Ill Gewerbeztg 1866, 23 Mondes, 1866, **11,** 138, J. C S. 1867, **20,** 317 Engineering, **15,** 17. Genie **38,** 270 See also Rev. d'Artill. 1872, **1,** 170. Ann Rep H M Inspec Expl 1887, 20.

[2] E P 1090, 1862 In E P 1297, 1863, J Bickford and G. Smith, guncotton, first treated with potassium silicate, is used as the center of a fuse

[3] E. P 2720, 1863. See E P 1300, 1865 The Lenk method of manufacture was described in the British Association for the Advancement of Science report of 1863, by F Abel, as follows

(1) The cotton employed is of superior quality, tolerably free from seed; it is carded loosely, twisted, and made up into skeins before conversion. The strands of the cotton composing the skeins are of two sizes — the larger being intended for cannon-cartridges, and the other for small-arms cartridges and bursters

(2) *Preparatory Preparation of the Cotton.* The cotton, made up into skeins weighing about 3 ounces each, is washed in a solution of pure carbonate of potassa of the specific gravity 1 02, being immersed in the boiling solution for a short time. Upon removal from the alkaline liquid, the skeins are placed in a centrifugal machine, by which the greater portion of the liquid is separated. The skeins are now washed in clear running water, either by allowing them to remain in it for three or four hours, or else by washing each skein by hand for a few minutes. They are then again worked in a centrifugal machine and afterwards dried—in summer by the rays of the sun, but during winter in a drying-house heated by air pipes to between 30° and 38° C.; the latter plan usually takes four or five days

(3) *Production of the Guncotton.* The nitric acid employed has a spec. grav. of 1.53 and the sulfuric acid a spec. grav. of 1 82. They are mixed in the proportion of three parts by weight of sulfuric acid and one part of

The earlier work of v. Lenk, from a chronological viewpoint,

nitric acid.

Two skeins (about 6 ounces) of the cotton are immersed at one time in the mixed acids, and moved about for a few moments with iron paddles. They are then raised upon a grating above the level of the acids and submitted to gentle pressure; thence they are transferred to covered stone jars, each of which receives six skeins of known weight. The jars are then weighed, some of the mixed acids being added if necessary, to bring the proportion of acids up to $10^1/_2$ lbs. to 1 lb of cotton

The jars are set aside for forty-eight hours in a cool place; in summer they should be placed in cold water. When that period has elapsed, the acid is separated from the cotton as far as possible by means of a centrifugal machine, as before described. The men working the machine are protected from the fumes of the acids by a wooden partition. The acids removed from the cotton are not used again in the preparation of guncotton.

The skeins of guncotton are at once removed from the centrifugal machine to perforated receptacles, which are immersed in a stream, where they are allowed to remain at least three weeks. Each skein is afterwards separately rinsed in the stream to remove mechanical impurities, and the water is then separated by the centrifugal machine.

The guncotton is next submitted to treatment with a solution of carbonate of potassa, as in the preliminary process, and again washed after the alkaline liquid has been expressed. When the skeins have been allowed to dry tolerably by simple exposure to air, they are placed in a large wooden tub containing a solution of silicate of soda, the temperature of which is about 15° C. This solution should have a specific gravity of 1.072, and is prepared as required from a solution of spec. grav. 1.216. The cotton remains one hour in the solution of silicate of soda, which is supposed to exercise two functions:

(a) That of protecting the cotton by acting as a varnish upon the fibers.

(b) That of retarding its combustion.

Upon removal of the guncotton from the bath of water-glass, the liquid is partly expressed by hand, and afterwards more fully by means of the centrifugal machine. The skeins must then be thoroughly dried. They are afterwards immersed in running water for five or six hours, and each subsequently washed by hand. The water having been extracted by the centrifugal machine, the guncotton is removed to the drying-house, where it remains eight or ten days. Its manufacture is then completed.

The guncotton is packed in ordinary deal boxes lined with paper, and kept in dry magazines until required to be made into cartridges, etc.

Well-organized arrangements are employed for mixing the sulfuric and nitric acids, immersing the cotton, and for conducting the various other operations connected with the manufacture.

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[1] J. Soc. Arts. 1863, **11**, 715; **14**, 47, 585. Brit. Assoc. Rep. No. 33, pp. 27, 33; abst. Jahr. Chem. 1864, **17**, 796, 798, 801.

[2] U. S. P. 43166, 1864; abst. Wag. Jahr. 1865, **11**, 410; Sci. Amer. July 9, 1864; Dingl. Poly. 1865, **178**, 145; Chem. Centr. 1866, **37**, 571; Poly. Centr. 1865, **31**, 1644.

is not clear. It seems that in 1852 the Austrian Emperor appointed a commission to inquire into the proposed application of guncotton for military purposes, which interruptedly continued to sit until 1865. In 1853 a factory was erected at Hirtenberg to exploit the Lenk method of manufacture, wherein the purification was more elaborate and thorough than in the original Schönbein process, for, instead of merely washing with water until neutral, v. Lenk washed continuously for three weeks, then boiled for several minutes with dilute potash solution, followed by impregnation with water glass and drying. Von Lenk constructed some batteries of twelve-inch guns to be used in testing the guncotton cartridges prepared by him, but the guns were soon so damaged by firing as to be worthless from the viewpoint of accuracy. About 1860 bronze guns replaced those previously used of iron, and these contained not only guncotton propulsive charge, but also had shells containing a bursting charge of the same explosive. Often, even these burst in the bore, evidently due to the very sudden shock.

The United States patent of v. Lenk contains a clear-cut description of his process. According to this, the cotton or other vegetable fiber is first spun into loose threads of sufficient strength to be easily handled (i. e., carded), then thoroughly boiled in a solution of potash or soda, washed and finally dried at 100° F. A mixture is made of one part nitric acid by weight, of 1.48-1.50 sp. gr., and three parts of common sulfuric acid, the mixture being allowed to stand until thoroughly mixed and cooled. The acid mixture is transferred to a three-compartment cast iron apparatus, one for the main bulk of the acids, one for the immersion of the cotton, and one for receiving the nitrated cotton. The cotton is next immersed in the nitrating acid in such a manner that every 3 oz. cotton must come in contact with 60 lbs. of the acid mixture.

The parcels thus dipped, after gentle pressing, are placed in the second compartment, where for each pound of cotton there must be 10.5 lbs. of acid mixture. The cotton is allowed to remain in contact with this acid for a minimum of 48 hours, meanwhile being kept at uniform temperature by cooling. The nitrated cotton is then pressed, centrifugalized to remove superfluous acid, placed in another wringer and thoroughly washed by a running stream of fresh water to remove "all the last particles of adhesive acids." The cotton is next removed, placed in a trough and secured in such a manner that a running stream of fresh water may pass through and over it for at least 14 days. To lessen the time of this operation the nitrocotton may be immersed in alcohol, boiled in a solution of common soap, washed and dried.

The nitrated cotton is next immersed in a solution of water glass (one lb. to 2 lbs. water) of 1.09 sp. gr., 0.198 lb. of this solution being added to each pound of nitrated cotton. The product is then taken out of the solution, exposed to the atmosphere for at least four days. This process has the tendency to preserve the material and to make its explosive qualities less rapid. The guncotton is again washed in soft water free of lime, and dried. It will be noted that this method has many points in advance of those processes heretofore disclosed. The water glass treatment, when properly made, added about 3% to the final weight of the nitrocotton.

Lenk claimed that where the French had failed was due to insufficient appreciation of the extreme care necessary in the washing process for elimination of the last traces of acid. J. Pelouze and Maurey[1] went over the entire subject in a painstaking manner, and eventually recorded their observations in a monograph.[2] They claimed the identity of the old French product with Lenk's guncotton, apparent from the "irrelevant" silicate treatment, and insisted on their formula, which required 12.16% N, and a weight increase of 177.78%. They maintained, contradictory to Lenk, that decomposition occurs more readily the higher it is nitrated. J. Russell[3] issued a favorable report on the Lenk process in 1864. In 1862 were issued the patents to B. Hotchkiss,[4] A. Johnston and L. Dow,[5] and E. Potter and J. Pomeroy,[6] for the use of guncotton in explosive cartridges, as well as the nitrostarch explosive of F. Uchatius, called Pyroxylam (see p. 1518).[1] The work of F. Hudson[2] was disclosed in 1861.

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[1] Compt rend. 1864, **59,** 363; Mech Mag 1864, **12,** 209; Ann chim. phys 1864, (4), **3,** 186, Chem. Centr. 1865, **36,** 193, 457, Wag. Jahr 1863, **9,** 310; 1864, **10,** 234, Bull Soc Chim 1864, **2,** 303; Poly. Centr 1865, **31,** 193; Phil Mag. 1864, (4), **28,** 535; Chem. News, 1864, **10,** 197, 210; Pharm. J. Trans. 1864, (2), **7,** 23; Jahr Chem 1864, **17,** 798; J. Pharm 1864, (4), **1,** 39; Amer. J. Pharm. 1865, **37,** 36, 221; Dingl. Poly. 1864, **174,** 209, 323; Les Mondes, 1864, **5,** 777. See Compt. rend. 1849, **28,** 110, 146.

[2] Pelouze and Maurey, Memoire sur la poudre-coton (pyroxyle), Paris, 1864, 80, pp. 41.

[3] Chem. News, 1864, **10,** 102; abst. Bull Soc. Chim. 1865, (2), **3,** 468; Jahr Chem. 1864, **17,** 801 Sci. Amer. **10,** 131; Mechan. Mag. **12,** 106.

[4] E. P. 1798, 1862.

[5] E. P. 2601, 1861.

[6] E. P. 679, 1862.

F. Abel and the Pulping of Guncotton. Preliminary to the discoveries of F. Abel, which were not communicated until 1865, appeared several papers which, in historical sequence, merit notice at this point. L. v. Karoli[3] investigated carefully the gases given off by the explosion of nitrocellulose, both in a vacuum and in a sealed tube, and made quantitative estimations of the NO, CO and CH_4 eliminated. G. Simpson obtained pure pyroxylin by precipitating an ether-alcohol solution of collodion and repeatedly washing. This was an efficient but expensive method of purification.[4]

C. Blondeau[5] expressed the opinion that cellulose in being converted into guncotton is changed into its isomeric modification, fulminose, which is the main constituent of parchment paper, and that the behavior of guncotton with ammonia is a confirmation of his view that it is an "ether tribasic alcohol," similar to cane sugar, the somewhat changeable compound being designated as nitrocellulosetriamide.

T. Sutton[6] described a guncotton soluble in absolute alcohol free from ether, called by him "alkalen," made by quick nitration at low temperatures, and alleged to be especially useful for photo-

[1] Dingl Poly. 1854, **132,** 371; Ber. Wein Akad. **10,** 748. Dingl. Poly. 1861, **161,** 146, Poly Centr. 1861, 1367, Poly Notiz 1861, 309; Wag Jahr. 1861, **7,** 234; Jahr Chem. 1861, **14,** 234, 901 Wag Jahr. 1862, **8,** 280. Wien acad. Ber **52,** II, 6, abst. Jahr Chem 1865, **18,** 783

[2] Dingl Poly. 1861, **162,** 156; Chem News, 1861, **4,** 105, 149; Jahr. Chem 1861, **14,** 901.

[3] Pogg. Ann. 1863, **118,** 544, Dingl Poly 1863, **168,** 158; **169,** 426, J. prakt. Chem. 1863, **90,** 129; Phil Mag. 1863, (4), **26,** 266, 272; Vierteljahrschaft. pr. Pharm 1864, **13,** 73, Wien Akadember. **47,** 59; Jahr. Pharm. **19,** 313; Chem. Centr. 1863, **34,** 596, Jahr. Chem. 1863, **16,** 744; Poly. Centr. 1863, **29,** 996; Wag. Jahr. 1863, **9,** 304; Bull Soc Chim 1866, **5,** 613.

[4] Amer. Chemist (2), **1,** 332; abst. Jahr Chem 1864, **71,** 1029, Poly. Centr. 1869, **35,** 753.

[5] Ann. Chim Phys. 1863, **68,** 462, Jahr Chem. 1863, **16,** 567. Compt. rend. 1864, **58,** 1011; J. prakt. Chem 1864, **93,** 318; Jahr. Chem 1864, **17,** 569; Instit. 1864, 195; Chem. News, **9,** 286; Chem Centr. 1865, **36,** 44. Compt. rend. 1865, **59,** 963; Chem. Centr. 1865, **36,** 476; Dingl. Poly. 1865, **178,** 166; Phot. Archiv. 1865, 342. Compt rend, 1865, **60,** 128; Chem. Centr. 1865, **36,** 476. Compt. rend. 1865, **61,** 378; Dingl. Poly. 1865, **178,** 147; Chem. Centr. 1865, **36,** 997; Chem. Tech. Rep. 1865, **4,** I, 116; Wag. Jahr. 1865, **11,** 412; Bull. Soc. Chim. 1865, **3,** 145; Deut. Ind. Ztg. 1865, 388; Mon. Sci. 1865, **7,** 898; Inst. 1865, 299; J. prakt. Chem. 1865, **94,** 317; **96,** 64; Poly. Centr. 1865, **31,** 1597.

[6] Rep. Chim. Appl. 1862, **4,** 145; abst. Jahr. Chem. 1862, **15,** 468, Chem. Centr. 1863, **34,** 1700. Am. J. Pharm. 1864, **36,** 20.

graphic purposes. E. Guignet[1] found that on boiling nitrocellulose for a prolonged time with an excess of ammonia, a brown solution is obtained consisting of acetic acid and an amorphous, brown nitrogeneous substance, hardly soluble in water, but soluble in acids and alkalis. The filtered solution contains a brown substance, precipitable by lead salts, and a considerable amount of ammonium nitrite and nitrate. In a later communication,[2] he obtained a glycose-like body with alcoholic KOH, while with alcoholic ammonia, an amorphous amido derivative results. He was unable to obtain Sutton's alcohol-soluble cellulose nitrate. Martin de Brettes,[3] O. Bernhard,[4] Belitski,[5] H. Krone,[6] A. Seguier, A. Morin and M. Chevreul,[7] J. Cartahu,[8] Wallis,[9] T. Tichanowitsch,[10] and R. Matthys[11] made contributions of comparatively minor importance.

The electrical properties of pyroxylin paper and guncotton were reported upon by J. Johnston in 1864,[12] the solubility in cuprammonium solutions by E. Mulder,[13] and the use for cartridges and explosive combinations by W. Newton and E. Shepherd,[14] I. Tice[15] and by E. Schultze.[16] Percy,[17] F. Varentrapp,[18] and

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[1] Compt rend 1863, **56,** 358; Chem Centr 1863, **34,** 689, Dingl. Poly 1863, **169,** 234, J prakt Chem 1863, **89,** 251, Zts Chem 1863, **6,** 191; Bull. Soc. Chim. 1863, **5,** 114, Jahr Chem 1863, **16,** 568, Poly. Centr 1863, **29,** 830.

[2] Compt rend 1885, **101,** 631; Jahr. Chem 1885, **38,** 1760, Wag. Jahr 1886, **32,** 319. Sabine, Les Mondes, 1864, **4,** 496 See also J Cartahu, Les Mondes, 1864, **4,** 582

[3] Compt rend. 1864, **58,** 665

[4] Buchners Rept Pharm. **12,** 440, Wag Jahr 1863, **9,** 659, Dingl Poly. 1864, **171,** 236, Poly Centr 1864, **35,** 410.

[5] Wieck's Gewerbeztg 1863, 64

[6] Bull de la Soc Fran de Phot. 1863, **9,** 128

[7] Compt rend 1864, **59,** 373, 374; abst Dingl Poly 1864, **174,** 220, 221. E. Mills, J C. S 1865, **18,** 319, Chem Centr. 1866, 229

[8] Les Mondes, 1864, **4,** 582 See also Sabine, Les Mondes, 1864, **4,** 496.

[9] Wieck's Gewerbeztg 1864, 320; Deut. Gewerbe Ztg 1864, No. 40; Chem Centr. 1864, **35,** 1590; Poly. Centr 1865, **31,** 1082

[10] Zts Chem. 1863, **6,** 550, 1864, **7,** 482; Jahr Chem 1863, **16,** 584 1864, **17,** 582, Chem Centr. 1864, **35,** 463.

[11] Les Mondes, 1864, **4,** 626

[12] Amer J. Sci 1864, (2), **37,** 115; Dingl Poly 1864, **171,** 462. Am J Sci. 1865, (2), **39,** 348. Aust.-Hung P. 387, 1887; abst Dingl. Poly. 1888 **267,** 370.

[13] Sheik Onderz. **3,** II, 157; abst. Jahr. Chem. 1863, **16,** 568.

[14] E. P. 2759, 1864.

[15] E. P. 881, 1863.

[16] E. P. 2353, 1863.

[17] Chem. Tech. Rep 1864, **3,** II, 113

[18] Dingl. Poly 1863, **169,** 77. Dingl. Poly. 1863, **169,** 234; J. prakt Chem 1863, **89,** 251.

J. Reynolds,[1] are among those investigators who also contributed.

When v. Lenk accepted the invitation of the British Association for the Advancement of Science to appear before a committee appointed by that body, and to answer such questions concerning his method of guncotton manufacture as they might choose to propound, and in order to aid him in explaining his system of manufacture, he brought over from Austria drawings and samples from the Imperial factory.[2] In addition to this source of information this committee had the advantages of the special services rendered by two of its members, e. g., Frankland, who was able by his own experiments to corroborate or refute many of the statements of Lenk, and Whitworth, who made experiments on the application of guncotton in mines, and had sent over to Austria rifles and ammunition to be experimented with by v. Lenk, with the view of obtaining results of use to the committee.

As the results of the hearings and investigations of this commission, the following conclusions were arrived at: First came the chemical considerations, including the manufacture of guncotton itself, and the answer to such inquiries as those which refer to its liability or non-liability to deterioration on keeping, the possibility of its spontaneous combustion, and the nature and effects of the products to which it is resolved on explosion.

As to the chemical nature of the material itself, their conclusions were that the v. Lenk guncotton differs from that usually made, in its conversion into a uniform, definite chemical compound. As was well known to chemists at that time, cotton when treated with strong nitric and sulfuric acids resolved itself into compounds varying considerably in composition and constitution, although they all contain the elements of nitric acid and are explosive to varying degrees. The most complete combination or product of substitution was that described by Hadow as $C_{36}H_{21}(NO_4)_9O_{30}$, identical with the trinitrocellulose of the Austrian chemists, $C_{12}H_2(NO_4)_3O_{10}$. While this is valueless for the purposes of transformation into collodion, it is Baron Lenk's guncotton, and as such, is obtained by the rigid exercise of certain manufacturing precautions, the principal among them being:

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[1] Phot. Arch. 1864, 184; Wag. Jahr. 1865, **11**, 322, Poly Centr. 1865, **31**, 336; Chem Centr. 1865, **36**, 363.

[2] G MacDonald, Arms and Expl. 1909, **17**, 23.

(1) The cleansing and perfect desiccation of the cotton as a preliminary to its immersion in the nitrating bath;

(2) Employment of the most concentrated acids;

(3) Steeping the cotton in a fresh, strong mixture of acids after its initial immersion and partial nitration;

(4) Continuation of the steeping for 48 hours;

(5) Thorough purification of the guncotton by several weeks' washing in running water, and,

(6) Finally, impregnation with an alkaline silicate as an antacid, and drying at a low temperature.

The committee makes a special note of the fact that, while at first blush the prolonged continuance of these processes may seem superfluous, it is really essential, because each cotton filament consists of a long tube, often twisted and even doubled up, and the acid has first to uniformly penetrate the inner depths of the individual filament, and afterwards removed by protracted washing. Hence the necessity of time. It appears to have been mainly the improper or insufficient recognition of these facts that the guncotton experimented on by the French gave irregular and unsatisfactory results. From the evidence submitted, it appears that the highest nitro compound when thoroughly freed from acid is not liable to some of the objections which have been urged against the compounds usually employed in experiments in guncotton formation.

These advantages may be classified as follows:

(1) The composition is uniform, hence the force of the gases generated on explosion may be accurately determined.

(2) It will not ignite until raised to a temperature of at least 136°, a heat which does not occur unless artificially produced by means which would render gunpowder also liable to ignition.

(3) There is a noticeably marked superiority in stability over other forms of guncotton, which have been kept unaltered over 15 years. Is not prone to that spontaneous slow decomposition which has been known to render lower products worthless after a short time. There are still more reasons for suspecting that even the guncotton produced by the Lenk process undergoes gradual deterioration, especially when exposed to the sunlight.

(4) There is one part of the process, the value of which is

open to doubt, i. e., the treatment of the guncotton with a solution of silicate of potash, it being considered that the amount of silica liberated by the carbon dioxide of the atmosphere is really of service in retarding combustion.

(5) Much apprehension has been felt about the effect of the gases produced by explosion of guncotton. It has been stated that both nitrous fumes and prussic acid are among these gases, and the point raised that the one would corrode the gun, and the other poison the artillerymen. In contradistinction, the gases liberated have been found to consist of N, CO_2 and CH_4 (light carburetted methane), all comparatively innocuous. And it is distinctly in evidence that practically the gun is less injured by repeated charges of guncotton than of gunpowder, and that the men are less affected by the fumes. The importance of this latter property in a confined area, as a fortress or ship, will be immediately apparent.

(6) An obvious disadvantage of this material as compared with gunpowder is that it explodes at a lower temperature, but against the greater liability of accident from this cause is the greatly diminished risk of explosion during drying, since guncotton is immersed in liquid, except in the final drying. The fact that guncotton is not injured by damp as is gunpowder, and is less hygroscopic, is one of its strong recommendations.

(7) A still more important chemical advantage is its perfect resolution into gases on explosion, so that there is no smoke to obscure the sight of the soldier who is firing, or to point out his position to the enemy. No residue remains in the gun to be removed before the next shot may be fired with safety.

In the practical application of the nitrocotton it is recommended that it be used in artillery in the form of spun thread or yarn. In this simple form it will conduct combustion slowly in the open air at a rate of not more than one foot per second, and when woven or spun into a texture or circular web of varying diameters, is suitable for the manufacture of common rifle cartridges, merely by cutting them into the proper lengths and enclosing them in stiff pasteboard cylinders which form cartridges. In this form its combustion in the open air takes place at a speed of ten feet per second. It is largely upon this report, and the character of those whose signatures are appended thereto, that may be said to mark the commencement of the reduction to mathematical terms of accuracy the stabilizing and manufacture of nitrocellulose for military purposes. E. Kopp,[1] and Redtenbacher, Schroetter and Schneider[2] have published critiques on this report.

E. Divers[3] kept guncotton in stoppered containers for two years, but on opening found much gas escaping, mostly NO. He considers the decomposition products to contain pectic and parapectic acids, but oxalic acid could not be detected.

Preliminary to the methods of nitrocellulose purification devized and put into execution by F. Abel, the 1862 patent of J. Tonkin[4] should be noted, in which the pulping of nitrocotton is described in detail. After describing the production of guncotton by his process of nitration, Tonkin says: "The cotton is to be washed in a continuous flow of water and well agitated or stirred therein, till the water does not indicate the presence of any acid. The cotton has now to be pressed to free it from water as much as is practicable, and in order to insure its being perfectly free from uncombined acid, it is dipped in a very weak solution of potassium carbonate (1 oz. of K_2CO_3 per gal. water). The fiber is then taken in the wet state and converted into pulp in the same manner as is practiced by paper makers, by putting the fiber into a cylinder having rapidly revolving knives." Although it is true that Tonkin does not *claim* the pulping of nitrocotton in his patent specification, his description is clear-cut and comprehensive. His pulped guncotton was mixed with sodium nitrate, charcoal and sulfur in the fabrication of explosives.

Previous to the granting of his patent for the pulping of nitrated cellulose, F. Abel had published results of his investigations in 1862,[5] 1863[6] and 1864,[7] in which latter year appeared

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1. Chem News, 1863, **7,** 141; abst. Rep. Chim Appl. 1863, **5,** 388. Mon Sci 1874, **16,** 499; Wag. Jahr 1874, **20,** 423.

2 Rept 33, Brit. Assoc Reports, 33; Jahr. Chem 1864, **17,** 797.

3. J C. S. 1863, **16,** 91, Chem Centr. 1863, 690; Proc Amer Pharm Assoc. 1864, **11,** 144; Jahr Chem 1863, **16,** 569; Chem. News, 1863, **7,** 154; Zts. Chem. Pharm 1863. 237; J. prakt. Chem. 1864, **91,** 58; Bull. Soc. Chim. 1864, **1,** 46 J S C. I. 1902, **21,** 297

4. E P. 320, 1862; abst. Mon Sci 1910, **72,** 728.

5. Chem News, 1862, **5,** 270; Rep. Chim. Appl. 1862, **4,** 262; Wag. Jahr. 1862, **8,** 273

6 Rep. Chim. Appl. 1863, 388; Württemberg Gewerbebl 1863, 417; Poly. Centr 1863, **29,** 1645. Wag. Jahr. 1863, **9,** 310.

7 Rep. No. 33, Brit Assoc. Rept , page 8; abst. Chem. Centr. 1864, **35,** 906; Jahr. Chem. 1864, **17,** 796.

his memoir in the Proceedings of the Royal Society on the inflammability and combustion of guncotton,[1] using the process of Lenk, the large-scale manufacture of which resulted in a yield of 177 parts, against a possible 183 parts on theory of trinitrate formation. He studied the luminous phenomena exhibited by the ignition of guncotton in small quantities in rarefied atmospheres, and the products of primary and secondary combustion.

In 1865 there was granted to Abel a patent for the pulping and compression of nitrocotton, by which its purity and hence stability were enhanced, and its speed of burning partially controlled by compression and superficial colloidation.[2] He first converted cotton into the nitrated form, using loose cotton rovings for this purpose. After the preliminary purification by washing in running water, followed by dilute alkali, transference was made to a beating engine similar to that used in the manufacture of paper from pulp, the guncotton pulp being then converted into solid masses, sheets and other forms by pressure. For high density, hydraulic pressure was applied to the guncotton. The prime points in the Abel method of guncotton treatment may be epitomized as follows:

(1) Reducing guncotton to a pulp, followed by pressure consolidation into the form desired, without the admixture of binding material.

(2) Admixture of nitrocellulose to the pulped guncotton, combining "soluble" and "insoluble" esters, in order to vary the ballistics of the explosive.

(3) Subjecting mixtures of various nitrocelluloses, either fibrous or pulped or both, to the action of solvents to effect their consolidation.

(4) The application to the surface of the consolidated guncotton of a solution of pyroxylin, shellac or other gum or resin.

Under the direction of F. Abel, at that time chemist of the English War Department, the manufacture of guncotton by this process was commenced on a comparatively small scale at the Royal Gunpowder Factory at Waltham Abbey. With governmental financial backing, it was possible for Abel to continue his investigations on a factory scale—researches, which in their entirety have revolutionized the manufacture of the cellulose nitrates, both those bodies of high and low nitration. In 1866[1] and 1867[2] he published his researches on guncotton, which contained a résumé of the essential steps in manufacture that had been put forward up to that time, and recited his extensive experimentation upon the problem of stability in a broad and comprehensive manner.

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[1] Proc Roy. Soc 1864, **13**, 204, Eng 1864, **17**, 349; Artiz. 1864, 151; Chem News, 1864, **9**, 206, 218; Jahr Chem 1864, **17**, 798, 801; Rept 33, Br. Assoc. Reports, 9

[2] E P. 1102, 1865; U S P 59888, 1866, F. P 69079, 1865 (Oct. 20). Add. July 18, 1868. J. Roy. U. S Inst 1865, **8**, 345.

The object of compressing the pulped guncotton was, of course, to restrain and modify the violence with which it exploded in the gun, but in this respect he was but partially successful, for the considerable number of accidents which still took place, showed that often the nitrocotton became uncontrollable, and exhibited a brisance considerably higher than anticipated. The use of guncotton at this stage, therefore, was confined to blasting purposes entirely, although in 1868 E. Brown found that dry guncotton could be readily made to explode by the use of a mercury fulminate detonator,[3] this observation having already been recorded by A. Nobel in respect to nitroglycerol.[4]

In the former (1866) contribution of Abel, the treatment of guncotton with water glass, forming such an essential feature of

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[1] Phil Trans. 1866, **156**, 269; Phil Mag 1866, **32**, 145; Proc. Roy. Inst. 1866, **4**, 245, 616; Chem. Centr. 1868, **39**, 443; Chem. News, 1866, **14**, 18, 250; Poly. Centr. 1866, **32**, 1231; Wag. Jahr. 1866, **12**, 294; Chem. News, 1866, **14**, 4; Deut. Ind Ztg. 1866, 254; Chem. Tech. Rep 1866, **5**, 102; Les Mondes, 1866, **12**, 664; Proc. Roy. Soc. 1867, **15**, 102; J. C. S. 1867, **20**, 310, 340; Pharm. J. Trans. 1867, (2), **8**, 67; J. prakt. Chem. 1867, **101**, 488; Dingl. Poly. 1867, **185**, 148, 154, 157; Jahr. Chem. 1866, **19**, 860; Poly. Centr. 1867, **33**, 1186.

[2] Phil. Trans. 1867, **157**, 181, J. C. S. 1867, **20**, 505; Phil. Mag. 1867, **33**, 545; Proc. Roy. Soc. 1867, **15**, 417; J. Roy. U. S. Service Inst. 1867, **10**, 417; Chem. News, 1867, **15**, 203; Poly. Centr. 1867, **33**, 283, 1186, 1414; Wag. Jahr. 1867, **13**, 329; Dingl. Poly. 1867, **185**, 148, 154; Chem. News, 1867, **14**, 250; Jahr. Chem. 1867, **20**, 912; Amer. J. Sci. (2), **44**, 288; Bull. Soc. 1867, (2), **7**, 527; Deut. Indust. Ztg. 1867, 202; J. prakt. Chem. 1867, **101**, 488; Les Mondes, 1867, **14**, 224; **15**, 689; Chem. Tech. Rep. 1867, **6**, II, 122; 1867, **6**, I, 120; Pharm. J. Trans. 1868, **9**, 386; Compt. rend. 1869, **69**, 105; Ann. Chim. Phys. 1870, **21**, 97. For discussion of above by A. Chariere, see Les Mondes, 1868, **16**, 143.

[3] F. Abel and E. Brown, E. P. 3115, 1868; abst. Deut. Industztg. 1868, 485; Chem. Tech. Rep. 1868, **7**, II, 149. See also Dingl. Poly. 1872, **206**, 500; Mechanics Mag. 1872, 478; Poly. Centr. 1873, **39**, 268; Deut. Industztg 1873, 38; Wag. Jahr. 1873, **19**, 355; Chem. Tech. Rep. 1873, **12**, I, 38.

[4] E. P. 1345, 1867; abst. Berggeist, 1867; Zts. Oest. Ing. Ver. 1867, 171; Deut. Indztg. 1867, 473; Bayer. Kunst. Gewerbebl. 1867, 732; Chem. Tech. Rep. 1867, **6**, II, 122.

v. Lenk's process, in accordance with the observations of Schrötter, Redtenbacher and Schneider, Pelouze and Maurey, was found to possess no important merits. The composition of the cotton experimented upon by Abel contained 0.044% ash, and C 44.26%, O 49.69%, and H 6.05%, while the ash of the guncotton made therefrom was invariably under 1%, with a hygroscopic moisture of 2%. The solubility in ether-alcohol in 20 factory runs was 1.3%-2.6%, with an average of 2.03%, and the mean nitrogen percentage 13.83.

His results are expressed in the following four generalizations:

(1) The guncotton was not prepared from *pure* cellulose, the most elaborate system of purification being inadequate, but from cotton separated from foreign matters as far as possible by the usual methods of purification adopted.

(2) Ample proof was furnished, by extensive and rigorous experiments, of the invariable existence in the purified guncotton (as produced by the most complete action of the strongest acids upon cotton, purified by treatment with alkali and washing) of notable proportions of substances which owe their existence to the presence of foreign matters remaining in the cotton fiber after its ordinary purification, and also the products resulting from the less perfect action of nitric acid upon small portions of the cellulose.

(3) Although these two varieties of impurities were extracted as far as possible, by repeated digestion with ether and alcohol, from the pyroxylin analyzed it was concluded that their complete removal by extraction was impossible.

(4) The existence of small amounts of these impurities tends to raise the percentage of carbon, reducing the proportion of nitrogen.

The second memoir on the stability of guncotton by F. Abel appeared in the Philosophical Transactions for 1867. The observations and experiments were carried out at Woolwich, and may be classed as having for their objects:

(a) Determination of the influence of light and of long protracted storage, under ordinary conditions as to temperature, upon the stability of guncotton;

(b) The investigation of the behavior of guncotton upon exposure, under varied conditions, to artificial temperatures, and to such elevated natural temperatures as are occasionally experienced in particular localities, and

(c) Examination of the influence exerted upon the stability of nitrocotton by special modes of preparing and preserving it.

The investigations, which occupy 72 pages in the Transactions, may be epitomized in the following ten subdivisions, and on account of their historical importance and technical significance, are produced herewith verbatim:

1. Guncotton produced from properly purified cotton, according to the directions given by von Lenk, may be exposed to diffused daylight, either in open air or in closed vessels, for very long periods without undergoing any change. The preservation of the material for 3½ years under those conditions has been perfect.

2. Long-continued exposure of the substance, in a condition of ordinary dryness, to strong daylight and sunlight produces a very gradual change in guncotton of the description defined above; and the statements which have been published regarding the very rapid decomposition of guncotton when exposed to sunlight do not, therefore, apply to the nearly pure trinitrocellulose obtained by strictly following the system of manufacture now adopted.

3. If guncotton in closed vessels is left for protracted periods exposed to strong daylight and sunlight in a moist or damp condition, it is affected to a somewhat greater extent; but even under these circumstances the change produced in the guncotton by several months' exposure is of a very trifling nature.

4. Guncotton which is exposed to sunlight until a faint acid reaction has become developed, and is then immediately afterwards packed into boxes which are tightly closed, does not undergo any change during subsequent preservation in ordinary storehouses (as far as the experience of 3½ years has shown).

5. Guncotton prepared and purified according to the prescribed system, and stored in the ordinarily dry condition, does not furnish any indication of alteration, beyond the development, shortly after it is first packed, of a slight peculiar odor, and the power of gradually imparting to litmus, when packed with it, a pink tinge.

6. The influence exercised upon the stability of guncotton of average quality, as obtained by strict adherence to von Lenk's system of manufacture, by prolonged exposure to temperatures considerably exceeding those which are experienced in tropical climates, is very trifling in comparison with the results recently published by Continental experimenters relating to the effects of heat upon guncotton; *and it may be so perfectly counteracted* by very simple means, which in no way interfere with the essential

qualities of the material, that the storage and transport of guncotton presents no greater danger, and is, under some circumstances, attended with much less risk of accident than is the case with gunpowder.

7. Perfectly pure guncotton, or trinitrocellulose, resists to a remarkable extent the destructive effects of temperatures even approaching 100° C.; and the lower nitro-products of cellulose (soluble guncotton) are at any rate not more prone to alteration, when pure. The incomplete conversion of cotton into the most explosive product does, therefore, not of necessity result in the production of a less perfectly permanent compound than that obtained by the most perfect action of the acid-mixture.

8. But all ordinary products of manufacture contain small proportions of organic nitrogenized impurities, of comparatively unstable properties, which have been formed by the action of nitric acid upon foreign matters retained by the cotton fiber, and which are not completely separated by the ordinary or even a more searching process of purification.

It is the presence of this class of impurity in guncotton which first gives rise to the development of free acid, when the substance is exposed to the action of heat, and it is the acid thus generated which eventually exerts a destructive action upon the cellulose-products, and thus establishes decomposition which heat materially accelerates. If the small quantity of acid developed from the impurity in question be neutralized as it becomes nascent, no injurious action upon the guncotton results, and the great promoting cause of the decomposition of guncotton by heat is removed This result is readily attained by uniformly distributing through guncotton a small proportion of a carbonate, the sodic carbonate, applied in the form of solution, being best adapted to this purpose.

9. The introduction into the finished guncotton of 1% of sodic carbonate affords to the material the power of resisting any serious change, even when exposed to such elevated temperatures as would induce some decomposition in the perfectly pure cellulose-products That proportion affords, therefore, security to guncotton against any destructive effects of the highest temperatures to which it is likely to be exposed, even under very exceptional climatic conditions. The only influences which the addition of that amount of carbonate to guncotton might exert upon its properties as an explosive, would consist in a trifling addition to the small amount of smoke attending its combustion, and in a slight retardation of its explosion, neither of which could be regarded as results detrimental to the probable value of the material.

10. Water acts as a most perfect protective to guncotton (except when it is exposed to sunlight), even under extremely

severe conditions of exposure to heat. An atmosphere saturated with aqueous vapor suffices to protect it from change at elevated temperatures, and wet or damp guncotton may be exposed for long periods in confined spaces to 100° without sustaining any change.

Actual immersion in water is not necessary for the most perfect preservation of guncotton; the material, if only damp to the touch, sustains not the slightest change, even if closely packed in large quantities. The organic impurities, which doubtless give rise to the very slight development of acid observed when guncotton is closely packed in the dry condition, appear equally protected by the water; for damp and wet guncotton which has been preserved for three years has not exhibited the faintest acidity. If as much water as possible be expelled from wet guncotton by the centrifugal extractor, it is obtained in a condition in which, though only damp to the touch, it is perfectly non-explosive; the water thus left in the material is sufficient not only to act as a perfect protective, but also to guard against all risk of accident. It is therefore in this condition that all reserve stores of the substance should be preserved, or that it should be transported in large quantities. If the proper proportion of sodic carbonate be dissolved in the water with which the guncotton is originally saturated for the purpose of obtaining it in this non-explosive form, the material, whenever it is dried for conversion into cartridges, or employment in other ways, will contain the alkaline matter required for its safe storage and use in the dry condition in all climates.

As has been previously indicated, developments in the manufacture of guncotton after 1863 were primarily along the lines of greater stability. The guncotton was reduced to pulp and the long washing in cold water was replaced by making the boiling of 15 minutes one of many hours. In 1863 the idea prevalent was that instability followed the retention of the nitrating acids. To lessen this Abel introduced the process of pulping in paper-making machines and subsequent washing in poachers.[1] Previous to this date Tonkin (loc. cit.) proposed to pulp guncotton to enable him to mix this material with the ingredients of black powder. This proposal did not anticipate the invention of Abel because the objects of the latter were to avoid the use of long-staple cotton and adopt cotton waste, the guncotton being mechanically converted into compact masses by pressure or granulation. Abel realized that the retention of the nitrating acids was not the sole cause of instability because in the British Association report of 1863 he said: "The guncotton may contain traces of nitro-compounds which are more liable to decomposition than it is itself." There is no doubt that the process of boiling to destroy these compounds was adopted many years later, but the exact date is not made definite in literature. On the 14th of August, 1871, there was a very serious explosion at the Stowmarket factory, when about 15 tons of guncotton exploded, destroying the factory and doing great damage in the town of Stowmarket. The Government's report on the cause of this explosion, dated 1872, clearly proves that boiling did not form a part of the Stowmarket processes, although they were working under Abel's patent of 1865. The cause of the explosion was ascribed to the spontaneous combustion under the accelerating influence of very hot weather, of some impure guncotton, containing about half a per cent. of sulfuric acid, this acid having been wilfully added by an unknown person after the guncotton had passed through the regular processes of manufacture and testing.

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[1] E. P. 1102, 1865.

The processes of manufacture in operation at Stowmarket in 1871 represent a very important step in the manufacture of guncotton, and for that reason its description should be interesting. The following details were published in the *Standard* newspaper soon after the explosion:

"The cotton used is the fine white waste from the cotton mills. After the bales are opened out in the receiving shed, the cotton, which is in loose rough tangle, is passed over to the first drying room, where it is well spread over open lattices, and subjected to a high temperature. After this it passes to the second drying room, also heated by the exhaust steam from the engines, where, when all moisture is thoroughly driven out, it is weighed into separate pounds and passed on through a box-tunnel to the dipping house. There is a long bench of tanks each about 14 inches wide, 2 feet 6 inches long, and 15 or 16 inches deep. These contain the mixed acid, viz., one part of nitric acid, with three times its weight of sulfuric acid. Into one of them each separate pound of cotton is dipped, stirred about for a few minutes, and is then taken out by an iron fork on to an open grate at the back of the tank, where the superfluous acid is partially pressed out by a hand lever with a plunger. The quantity of acid absorbed in each operation is about 10 lbs. or 11 lbs., and this is replaced after each dipping. Each workman has 4 tanks to attend, and he places the 1-lb. batches of cotton in one tank after the other, taking them out in the same order and filling up as he goes on. The pats, sufficiently pressed to prevent dripping, are next carried on to the soaking house, where they are put separately into earthen pots about 8 or 9 inches deep and 7 inches in diameter, with overhanging lids, and standing about three-quarters of their height in water. The cotton here stands for twelve hours, the object being to convert the particles and portions of the cotton which had escaped conversion in the first dipping process; there being still amply sufficient acids in the mass to continue the chemical action upon the unchanged fibers. The heat generated in this operation is considerable, and smouldering not unfrequently sets in, but is stopped by a little addition of acid. These pots are replaced and refilled in rotation as the digested cotton is taken away to the centrifugals. The centrifugal machines are arranged in sets of four in an adjoining house, and consist of good-sized coned discs, surrounded with a wire or perforated screw; they are set horizontally with their shafts vertical. These work within protecting cylinders, and are driven by level wheel gearing and pulleys at the rate of 1,500 or 2,000 revolutions per minute. Six of the pots are emptied into each centrifugal, the charge being broken up and uniformly distributed before the disc is set spinning.

"The moment the driving gear is put on, the cotton flies out towards the wire screw, and the acid is whirled out through the meshes like water from a trundling mop. This operation is continued until the dripping of the acid ceases, when the machine is stopped and its contents hooked out by iron forks into an iron pan, are carried smoking with red fumes and 'copped' or tipped into the water tub, which is a round wooden iron-hooped article, about 3 feet 6 inches deep and 4 feet in diameter, stuck low down in the river bank, with a spout of water constantly running into it. Only one charge from the centrifugal is put in at a time, that is, 6 lbs. of the original cotton, now converted into guncotton, and each charge remains in the washing tub during the time the following charge is being dealt with in the centrifugal. The object of this immersion is to arrest chemical action, to overcome the heat, and, as much as possible, to wash out the acid. . . . .

"From the tubs the charges are thrown into a large tank about 10 feet long, 6 feet wide, and 4 or more feet deep, through which a current of water coming in near the top at one end flows out through the bottom at the other. From this tank the supply of guncotton for the subsequent operations on the other side of the grounds is taken. The cotton rests in it from 24 to 12 hours, that is to say, it is filled by a day's work, and emptied by the next day's requirements. If into this tank any acid guncotton is put the contained acid will be mainly sulfuric, the nitric of the original dipping having been absorbed by the cellulose. . .

"We will now follow the cotton through its finishing stages in the second part of the factory. Taken from the first tank, the cotton is carried to another series of centrifugals, or rather to four centrifugals and their tanks. Passed through the first centrifugals until the water leaves off running it goes into the second tank, thence into the second centrifugal, then into the third tank, again into the third centrifugal, next to the fourth tank, and finally at this stage into the fourth centrifugal.

"Each charge, as it is finished, is carried on a wooden beck by hand to the beater engines, which by means of their bevelled knives and knifed roller first break the clots, and then the beater being screwed to adjustment, the cotton is pulled and lacerated into a pulp, which as finished runs away by a trough into the poacher, the wheel in which stirs it up continually for some time. When the pulp is sufficiently treated it is run off through a valve by a wooden trunk into an empty tank about ten feet long and of similar dimensions to the first receiving tank.

"The poacher house is one large, long, spacious building, clear, that is, unpartitioned from end to end, so that everyone in it can see along its entire length and extent. The poachers, which are large oval troughs about twelve feet long, eight feet wide and four feet six inches deep, have at one side, extending halfway across the breadth of the trough, a large wooden wheel like that of a water mill, which revolves, dragging the pulp in on one side and turning it out on the other, so that it is thus kept in commotion, a man also stirring it up occasionally from the bottom. The pulp is covered over by about two feet of water with which it more or less commingles. There are pipes also for letting in water and running it off. At this stage the alkali and the lime are added. It is from these poachers that the samples are taken for the chemists tests."

To this description should be added that while the guncotton was in the poachers, burnt lime and sodium carbonate were added so that $1\frac{1}{2}\%$ to 2% of calcium carbonate was left in the finished guncotton.

The product had to pass the following heat test:

Apparatus Required. A shallow oil bath, having a loose cover of sheet tin, which rests about one inch above the oil and has perforations of proper dimensions to receive a test tube and a thermometer. Suitable heating arrangements for raising the temperature of the oil from 150° to 170° Fahrenheit in from 10 to 13 minutes. A thermometer and a glass test tube; the latter is about 6 inches long, and $^{11}/_{16}$ of an inch in diameter and is provided with a loosely fitting cork through which passes a slender glass rod about 6 inches long. A small dropping tube or wash bottle, containing distilled water.

Materials Required. The *test paper* is prepared as follows:

45 grains of white starch are added to $8^1/_2$ ozs. of water, and the mixture is stirred and heated to boiling; 15 grains of iodide of potassium are dissolved in $8^1/_2$ ozs. of water. The two solutions are thoroughly mixed together. Strips or sheets of white filter paper are dipped in the solution thus prepared; they are then allowed to drain and dry. The dimensions of the pieces of test paper used are about $^1/_2$ an inch to $^5/_8$ inch.

The guncotton to be tested is removed from the compressed mass by gentle scraping; 4 grains of the air-dry substances are used in the test.

Application of the Test. The thermometer is fixed so as to be inserted through the lid of the bath into the oil, to a depth just sufficient to cover the bulb. The specimen to be tested is inserted into the test tube, and gently pressed down to the bottom. A test paper is fixed on to the lower extremity of the glass rod, so that, when inserted into the tube, it will be in a vertical position. A drop of distilled water is applied to the upper edge of the test tube; the quantity used being only sufficient to moisten about *two-thirds* of the paper. When the temperature of the bath has been raised to about 115° F., the corked test tube is inserted through the perforation in the cover, and is immersed in the oil to the same depth as the thermometer. A ring of moisture will presently be deposited in the test tube a little above the cover of the bath; the position of the test paper is then adjusted in the tube by lowering or raising the glass rod, until the lower margin of the moistened part of the paper is on a level with the bottom of the ring of moisture in the tube. The paper is then closely watched. The test is complete when a bluish brown coloration makes its appearance at the line of boundary between the dry and moist parts of the test paper. This coloration must not appear at any temperature below 190° F.

In 1867 F. Abel conducted extensive investigations upon the effect of alkalis upon nitrocotton, he having observed on several occasions that the nature and amount of mineral impurities exerted great differences upon the rapidity with which the substances sustained alteration upon exposure to heat. Some samples, which were heated for comparatively long periods without exhibiting signs of deterioration, were found to contain much larger proportions of calcium and magnesium carbonates than specimens with which in other respects they apparently were identical.

This observation led to careful investigations of the comparative effects of temperatures of 90°–100° upon a number of lots of guncotton, the percentages of alkaline earth carbonates ontained therein of which were known. Experiments made with hese "alkalized" guncotton in the main indicated that the resence of small quantities of the alkali and alkaline earth caronates, appeared to act as ant-acids, and hence stabilizers, but o definite results were obtained as to the maxima or minima mount of a named carbonate, the presence of which gave most esirable results. Other factors in guncotton stability in addition o the presence of carbonates undoubtedly were present, and aparently in sufficient but variable amounts to admit of no clearut and comprehensive generalizations. Numerous samples of itrated cotton which had been "silicated" (treated with water lass) varied greatly in their powers of resisting change at comaratively high temperatures, and it was demonstrated that they ere invariably rendered decidedly more prone to change if thorughly washed in distilled water previous to their exposure to eat. He found that a very small proportion of carbonate would xert a notable influence upon the power of guncotton in resisting he effects of heat.

In 1874 F. Abel contributed a memoir on the history of xplosive agents,[1] in which is epitomized and frankly discussed he results which had contributed permanence to the state of he art up to that time.[2] He developed that the facility with which an explosion accomplishes detonation is proportionate to the mechanical force and heat developed by that explosion, and that there exists a certain similarity or synchronism of the vibrations developed by the explosion of particular substances which operate in favoring the detonation of another substance. While, in the absence of such synchronism, a much more powerful initial detonation, or the application of much greater force, would be required to effect the detonation of the material operated upon. This view was supported by P. Champion and H. Pellet.[1] Abel clearly differentiated between explosion, as distinguished from development of detonation, and violence of transmitted concussion. The manner in which resistance to mechanical motion favors the chemical disintegration or explosion of the portions of a compact mass of guncotton when subjected to a blow, as from the impact of a bullet, was conclusively demonstrated by a series of experiments with guncotton disks of identical density and diameter, differing in thickness, and hence in weight.

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[1] Phil. Trans. 1874, **164,** 337; Compt rend 1874, **78,** 1227, 1301, 362, 1432; 1874, **79,** 204, 294, 360; Ann. Chim Phys 1874, **2,** 170, 1874, , 268. Mon. Sci, 1874, **16,** 595; Roy Eng Papers, 1844, **22,** 90; Proc. Roy. oc. 1874, **22,** 408; Dingl Poly. 1874, **213,** 174, 374; 1875, **215,** 123, 341; hem Tech. Mitth. 1874–1875, 101; Ber. 1874, **7,** 742, Les Mondes, 1874, **5,** 597; Eng. Vm. **38,** 342; Proc Roy. Soc. 1879, **29,** 123, Compt rend. 1879, **9,** 155, Phil. Trans 1880, **171,** 203

[2] Ber. 1868, **2,** 314; Chem. Tech Rep. 1868, **7,** II, 149 Phil Trans. 869, **159,** 489; Poly. Notiz. 1869, **24,** 353, Poly Centr 1869, **35,** 1245; Compt. nd. 1869, **69,** 105; Proc. Roy Soc 1869, **17,** 395; J C S 1870, **23,** 41; on. Sci. 1869, **11,** 902; Wag. Jahr 1869, **15,** 264; Mon Sci 1871, **13,** 662, 25; J. Soc. Arts, 1879, **27,** 437 Dingl Poly. 1871, **202,** 374, Chem News, 871, **24,** 141; Chem. Centr. 1871, **42,** 764, Jahr. Chem 1871, **42,** 764, 1030; er. 1871, **4,** 883; Poly. Centr. 1871, **37,** 1375; 1872, **38,** 883 Mechanics ag. 1872, 443; Wieck's Gewerbeztg. 1872, 73, Roy. Inst. 1872. J. Roy. . S. Inst. 1865, **8,** 345; 1873, **16,** 457. Pharm J. Trans. (3), **3,** 565, 583; ahr. Chem. 1873, **26,** 1027. Poly. Centr. 1875, **40,** 60 Rev. d'Artill 1875, , 256. Inst. C. Eng. May 14, 1872; Mech. Mag. 1872, 419; Amer. Chemist, 872, **3,** 264, 419; 1873, 310; J. de Pharm. et Chim., Oct. 1872, (4), **16,** 261; **9,** 273. Poly. Centr. 1875, **40,** 60; Pop. Sci. Month. 1875, **7,** 247. Compt. nd. 1876, **83,** 707, 1011; Ber. 1876, **9,** 1939; Jahr. 1876, 1111; Chem. Centr. 876, **84,** 739; 1877, 84; J. C. S. 1877, **31,** i, 453; Bull. Soc. Chim. 1877, (2), **9,** 27. Chem. News, 1877, **35,** 10, 155; Wag. Jahr. 1877, **23,** 385; Pharm. . Trans. **6,** 71; **9,** 386. Bull. de la Soc. Franc. de Phot. 1872, **18,** 40; 1877, **3,** 108. Chem. News, 1879, **39,** 34, 165, 177, 187, 198, 209; Mon. Sci. 1879,

Nitrocellulose Development, Period 1865–1870. The investigations of Abel previously briefly abstracted, were of far-reaching and enduring consequence, in that, in conjunction with the perseverence of von Lenk, and the solidity which was imparted to the subject by the favorable report by the British Association Committee, public distrust and Governmental apathy were removed and a recrudescence ensued, a resurgence which has augmented up to the present time.

The impetus imparted to the subject by the researches of Abel, naturally stimulated other investigators to critically ex-

21, 454, 1057. Wag. Jahr. 1879, **25,** 422; Mondes, **49,** 427. J. Frank. Inst. 1886, **79,** 37, 133, 189. Dingl. Poly. 1865, **178,** 145; abst. Sci Amer. July 9, 1864 Chem Tech Rep 1879, **18,** I, 287 E. P. 1470, 1888, D. R. P. 11030, 1880; abst Proc U S. Nav. Inst 1889, **15,** 213; J. A C. S. 1881, **3,** 74. E. P. 4179, 1875 Dynamite Manufacturing Co, E. P. 2519, 1878, F P. 127843, 1878; abst. Mon. Sci. 1879, **21,** 1047. A. Nobel and F. Abel, Rev. d'Artil 1879, **15,** 134; Jahr. Chem. 1880, **33,** 1307; Dingl Poly 1876, **221,** 94; Ber. 1876, **9,** 650; J. Pharm. Chim. (4), **30,** 426. R. Bottger, Ber. 1869, **2,** 609. Deut. Ind. Ztg. 1873, 18; abst. Wag. Jahr. 1873, **19,** 356. Jahr. Phys. Verr. Frankfurt 1872–1873, 10; 1877–1878, 23; abst. Chem Centr. 1874, **45,** 346; 1879, **50,** 750; Ber. 1876, **9,** 1795. G. MacDonald, Arms and Explos. 1909, **4,** 135, 150; 1910, **5,** 10, 66; abst. C. A. 1910, **4,** 384, 1101, 2205; J. S. C. I 1911, **30,** 241, 251; Zts. Schiess. Spreng. 1911, **6,** 389.

[1] Compt. rend. 1872, **75,** 210; abst. Chem. Centr. 1872, **43,** 562; Wag. Jahr. 1872, **18,** 300; Poly. Centr. 1872, **38,** 1493; J. C. S. 1872, **25,** 874; J. Pharm. Chim. 1872, **16,** 189, Amer Chemist, 1872, **3,** 272; 1873, **3,** 374; Mon. Sci. 1872, **14,** 672; Bull. Soc. Chim. 1872, **18,** 392; Dingl. Poly. 1872, **206,** 154; Jahr. Chem. 1872, **25,** 98.

amine the different angles and various phases of the von Lenk process and its possibilities. H. Melsens[1] went over the subject critically, and adduced that a little ammonia or dilute sodium hydroxide should be used in the final washing process, and that it is advizable that guncotton should be kept dry and cool to minimize proneness to deterioration. W. Scott,[2] Dietzenbacher,[3] Kral,[4] A. Vogel,[5] and J. Stas,[6] published independently in 1865 general contributions on the subject. In this year also appeared the blasting preparation of C. Reichen,[7] composed of paper impregnated with potassium chlorate, nitrate, ferrocyanide and chromate, covered with a solution of nitrocotton in acetic acid.

The ensuing year brought forth the Haloxylin of W. and E. Fehleisen,[8] containing nothing essentially new. The spectroscopic examinations of collodion made by Rutherford,[9] and the blasting cartridge manufacturing processes of W. Dixon,[10] and of A. Rollason,[11] brought forth nothing novel. F. Reeves and J.

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[1] Bull Soc Chim 1865, **3,** 34, Wag Jahr 1865, **11,** 412, Bull d'Enc 1866, 25, Instit 1865, 293, Jahr Chem 1864, **17,** 801, 1865, **18,** 785, Chem Centr 1865, **36,** 1167, Mon Sci 1866, **18,** 346

The pyrotechnic composition of J Fredureau and H de Chavannes, E P 3359, 1865, was a flame producing composition of xyloidine or guncotton admixed with resins, sawdust, lycopodium and chlorates, and intended for indoor use

[2] Rept Brit Assoc Adv Sci 1865, 35, Chem Tech Rep 1866, **5,** I, 102, J prakt Chem 1867, **101,** 447, Chem Centr 1868, **39,** 444; Jahr Chem 1867, **20,** 914, Bull Soc Chim 1867, (2), **9,** 383

[3] Compt rend 1865, **60,** 1022, Dingl Poly 1865, **178,** 229, Chem News, 1865, **11,** 250, J Pharm Chim 1866, **2,** 227, Jahr Chem 1865, **18,** 151

[4] Chem. Centr 1865, **36,** 258, Poly Centr 1865, **31,** 1519; Wag. Jahr 1865, **11,** 413, Wieck's Gewerbeztg 1865, 355

[5] Chem Tech Rep 1865, **4,** II, 72, Phot Mitth 1865, 111; Chem Tech Mitth 1865–1866, 37 N Rep Pharm **21,** 6, J C S 1872, **25,** 272. N Rep Pharm. 1872, 7, Dingl Poly 1872, **203,** 504, Jahr Chem 1872, **25,** 1083, Poly Notiz 1872, No 4, Pharm Centralh 1872, **14,** No 17, Chem. Tech Mitth 1871 1872, 48 Bull Soc Franc de Phot 1873, **19,** 35. Les Mondes, 1873, **30,** 132

[6] Berggeist, 1865, No 27, Dingl Poly 1865, **176,** 165

[7] E P 2266, 1865 See Darapsky, Poly Centr 1865, **31,** 680, Dingl. Poly. 1865, **175,** 451, 1869, **192,** 165, 405, Poly Centr 1869, 1193, Poly. Notiz 1869, 156; Kurhess, Gewerbebl 1869, 59, Mechanic's Mag 1869, 240; Wag. Jahr. 1869, **15,** 257

[8] Bavarian P. Feb. 5, 1866, abst Poly Notizbl 1880, **35,** 40 Described by G Neumeyer, Deut. Ind Ztg 1866, 48, 277; 1867, 77, 448, Dingl. Poly. 1866, **182,** 248, 251; 1867, **184,** 163, Poly Centr 1867, **33,** 674; Chem Tech. Mitth. 1866–1867, 251, Wag. Jahr 1866, **12,** 233; 1867, **13,** 245. E. P. 1341, 1866. This powder contains no nitrocellulose, but powdered cellulose or sawdust.

[9] Bull. Soc. Franc. de Phot 1866, **12,** 262.

[10] E. P. 845, 1866.

[11] E. P. 3301, 1866.

Muschamp[1] disclosed their process for making guncotton from old rags by boiling, shredding, bleaching, nitrating and pulping, but no mention is made as to the stability of the product. The influence of the oxycellulose nitrates upon the keeping qualities of nitrocotton was imperfectly appreciated at that time.

There was granted patent protection to E. Prentice in 1866 for a series of applications of[2] nitrated cellulose, which deserves more than a casual notice herein. He combined 15% of cotton and the balance guncotton into a homogeneous mixture by pulping,[3] and employed the mixture as a propelling charge in guns, waterproofing the charge by the addition of paraffin,[4] beeswax,[5] or rubber.[6] The collodion of Reissig[7] was announced.

In the biennial period of 1867–1868 appeared the patented process of A. Tronchon,[8] L. Bruen,[9] H. Garret and G. Holcroft,[10] and J. Reeves,[11] for the manufacture and waterproofing of guncotton cartridges, and the methods of G. Clark[12] and of C. Ditt-

[1] E. P. 3293, 1866.

[2] Les Mondes, 1866, **11**, 6, 600. Chem. Tech. Rep. 1867, **C**, I, 129; Zts. V. dt. Ing. 1868, 584; Deut Industztg. 1868, 8; Wag Jahr. **14**, 358; Chem. Centr. 1869, **40**, 72; Mech. Mag. **14**, 219, 231. Hall, Chem. Tech. Rep. 1874, **13**, II, 198. J. Hall, E. P. 2772, 1872; abst. Wag. Jahr. 1874, **20**, 424; Ber. 1874, **7**, 743; Bull. Soc. Chim. 1874, **22**, 141. J. Hall & Son, Mechanic's Mag. Apr. 1847; Dingl. Poly. 1847, **104**, 465. Jahr. Chem. 1847–1848, 1143; Liebig and Kopp's Ann. Report, 1847–1848, **2**, 376. See also Wilson and Prentice, Dingl. Poly. 1868, **189**, 78; Poly. Centr. 1868, 1277; Mon. Sci. 1868, **10**, 640; Chem. News, 1868, **17**, 195; Wag. Jahr. 1868, **14**, 357.

[3] E. Prentice, E. P. 953, 1866. F. P. 71285, 1866.

[4] E. Prentice and T. Richardson, E. P. 1129, 1867.

[5] E. Prentice, E. P. 2768, 1877; abst. Dingl. Poly. 1878, **230**, 188; Ber. 1878, **11**, I, 1390; Wag. Jahr. 1878, **24**, 466; Chem. Tech. Rep. 1878, **17**, I, 355. E. P. 174, 1877.

[6] F. Prentice, E. P. 3127, 1867.

[7] Dingl. Poly. 1866, **182**, 348; Hamburg. Gewerbebl. 1866, No. 42; Chem. Tech. Mitth. 1866–1867, 30.

[8] E. P. 1002, 1867.

[9] E. P. 1216, 1867.

[10] E. P. 2923, 1867.

[11] E. P. 989, 1867.

[12] E. P. 3408, 1868. See Mon. Sci. 1870, **12**, 63; Deut. Ind. Ztg. 1870, 48; Wag. Jahr. 1870, **16**, 217. See also: W. Gintl, Wien. Akad. Ber. 1869, **59**, 809; Bull. Soc. Chim. 1869, **13**, 435; J. prakt. Chem. 1869, **107**, 478; Poly. Centr. 1870, **36**, 159; Zts. Chem. 1869, **5**, 703; Pharm. Zts. Russ. Nov. 1870, Proc. Amer. Pharm. Assoc. **19**, 261. Ber. ueber die Zuendwarren, 1874, 31. A. Girard, Bull. de la Soc. Fran. de Phot. 1867, **13**, 203; Compt. rend. 1868, **67**, 820; Jahr. Chem. 1868, 771; Zts. Chem. 1868, 66; J. prakt. Chem. 1869, **107**, 266; Bull. Soc. Chim. 1869, (2), **11**, 498. Bull. de la Soc. Fran. de Phot. 1870, **16**, 41. Compt. rend. 1876, **82**, 1105; Dingl. Poly. 1876, **219**, 549. Compt. rend. 1879, **89**, 170; J. C. S. 1879, A, **36**, 911; Jahr. Chem. 1879, 1116; Publ. Ind. **26**, 46. H. Grothe, Poly. Centr. 1870, 641; Dingl. Poly. 1870, **196**, 553.

mar[1] for the use of nitrocellulose in connection with nitro glycerol for the formation of a plastic like dynamite. The nitrated paper of Freund,[2] the dry collodion of Barnes[3] and of Liesegang,[4] and the miscellaneous contributions of G. Merz,[5] O. Kreig,[6] W. Grüne,[7] J. Latham,[8] E. Schunk,[9] Reese,[10] F. Sussner,[11] together with the nitroglucose experiments of C. Lea,[12] epitomize the trend of advancement.

In 1869 appeared the process of E. Monckton[13] for combining gunpowder and guncotton as an explosive, and the rubber-like mass of A. Baeyer,[14] formed by heating PCl_5 and $POCl_3$ with guncotton, the latter dissolving without browning. O. Popp[15] isolated from the root bulbs of Synanthereae a new carbohydrate, Synanthrose, which nitrated to nitrosynanthrose, an almost white body, insoluble in alcohol and water, and is explosive. The same year appeared the results on nitrocellulose communicated by Joy,[16] L. Troost,[17] Stroblberger,[18] F. Mussgiller,[19] and J. Dougall, on the application of the "Schultze granulated wood powder."[1]

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[1] E. P. 3458, 1867; 3088, 1875. Dingl. Poly. 1870, **196,** 89; Chem. Centr. 1870, **41,** 366; Bull Soc Chim. 1870, (2), **14,** 349; Jahr. Chem. 1870, **23,** 1128; Amer. Artiz 1870, 96; Chem News, 1870, **21,** 275; Poly Centr. 1870, **36,** 930; Deut. Industrieztg. 1870, 115, Wag. Jahr 1869, **16,** 256; 1871, **17,** 217. See also A. Nobel, Dingl Poly 1869, **192,** 405; abst. Chem. Tech. Rep. 1869, **8,** I, 104.

[2] Bull. Soc. Franc. Phot. 1867, **13,** 269, Wieck's Gewerbeztg. 1867, 410

[3] Bull. Soc. Franc. Phot 1867, **13,** 232.

[4] Bull. Soc. Franc. Phot. 1867, **13,** 23.

[5] J. prakt. Chem 1867, **101,** 261; Chem. Centr. 1868, **39,** 99.

[6] Ver. Deut. Ing. 1868, **12,** 584; Dingl. Poly. 1868, **190,** 253; Gewerbebl. Wurttemberg, 1868, **18,** 508; Poly. Centr. 1869, **35,** 72.

[7] Phot. Mitth. **4,** 50, abst. Chem. Tech. Rep. 1867, **6,** I, 75.

[8] J. Roy. U. S. Inst. 1867, **10,** 328.

[9] Dingl. Poly. 1868, **189,** 78; Chem. News, 1868, **17,** 195.

[10] Phot. Jahr. **14,** 97.

[11] Oesterr. Zts. Berg. u. Hüttenwesen, 1867, No. 14; abst Poly. Centr. 1867, **33,** 998.

[12] Chem. Tech. Rep. 1868, **7,** II, 113; J. prakt. Chem. 1868, **105,** 191; Amer. J. Sci. 1868, (2), **45,** 381; Zts. Chem. 1868, **11,** 532; Bull. Soc. Chim. 1868, (2), **10,** 506; Jahr. Chem. 1868, **21,** 760.

[13] E. P. 2944, 1869

[14] Ber. 1869, **2,** 54; Zts. Chem. 1869, 345; Bull. Soc. Chim. 1869, **12,** 292; Jahr. Chem. 1869, **22,** 742.

[15] Ann. 1870, **156,** 181; abst. Chem. Centr. 1870, **41,** 787; Jahr. Chem. 1870, **23,** 845; Ber. 1871, **4,** 57; J. C. S. 1871, **24,** 348; Bull. Soc. Chim. 1871, **15,** 96.

[16] Sci. Amer. **24,** 22.

[17] Rec. de cours. Sci. 1869, 274.

[18] Gewerbebl. Würtemb. 1869, 251; Poly. Centr. 1869, **35,** 617; Chem. Tech. Rep. 1869, **8,** I, 78.

[19] Proc. Amer. Pharm. Assoc. 1870, **18,** 271; Amer. J. Pharm. 1870, **42,** 145.

From the contributions appearing in 1870, may be mentioned those of Malderen,[2] Radbruch,[3] P. Fresenius,[4] and of Camuzet. The treatise on guncotton by H. Dussauce appeared in 1869.

Cellulose Nitrate Advancement, Period 1871–1880. This ten-year period is replete with a large number of comparatively unimportant steps in advancement, which isolated, do not individually appear as being especially noteworthy, but which in their entirety, as viewed from the perspective of a half-century of elapsed time, indicate a distinct and permanent tendency to stabilize, popularize and commercialize the art upon an enduring footing.

In 1870 appeared the R. Punshon powder,[6] combining guncotton with un-nitrated carbohydrates, as sugar. The following year Davis,[7] V. Magendie,[8] A. Fisher[9] and Bartholomew,[10] published contributions, and L. Bleekrode found for some cellulose nitrates, that when saturated with combustible liquids,[11] upon ignition, the liquid burned, the guncotton often melting like snow, but without deflagration.

P. Champion alone[12] and with H. Pellet,[13] carried on extensive experiments on the explosion of compressed guncotton, and found that the higher nitrated celluloses, when substantially dry, may be detonated with a brass cap with 0.2 mm. wall thickness and 2 gm. mercury fulminate. E. Zettnow[1] made a series of experiments for the purpose of finding a way of preparing nitrocellulose which always gives collodion—a laudable but impossible task—in experimentally going over the processes of his contemporaries and predecessors in detail. His results are interesting, but especially applicable to the lower nitrated photographic collodions.

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[1] J Roy. United Service Inst 1869, **12**, 127.

[2] Phot Jahr **17**, 93

[3] Wieck's Gewerbeztg 1870, 48

[4] Dingl Poly 1871, **199**, 247, Naturf 1871, 89; Poly Centr 1871, **37**, 408; Poly Notiz 1871, **26**, 33

[5] Bull de la Soc Franc. de Phot 1870, **16**, 35 Mon Sci 1870, **12**, 424, 425.

[6] E P. 2867, 1870, 4268, 1875, F. P. 91749, 1871 J Soc. Arts, 1872, **20**, 186, 427.

[7] Phot Jahr **18**, 25, 37

[8] Rept. H M. Inspec Exptl Aug 11, 1871, Mar. 7, 1877; Nov. 3, 1882, **43**.

[9] J. Roy. U. S Inst. 1871, **14**, 419.

[10] Phot. Jahr **18**, 12 M Sokoloff, Ber 1879, **12**, 688, 698; J. C. S. 1879, **36**, 777, 1080, Chem Tech. Rep 1879, **18**, I, 286; Chem. Centr. 1870, 374; Wag Jahr. 1879, **25**, 423, Bull. Soc Chim. 1880, (2), **33**, 165; Jahr Chem. 1880, 1026; Year Book Pharm 1880, 80, Gewerblatt, **12**, 688, 698; Pharm. Centr. **20**, 277.

[11] Phil. Mag. 1871, **41**, 39, 162; Dingl. Poly 1871, **200**, 338; J. C. S. 1871, **24**, 171; Naturforscher, 1871, No 20; Poly. Centr. 1871, **37**, 923, Poly. Notizbl. 1871, **26**, 155; Chem. Centr. 1871, **42**, 225; Deut Ind. Ztg. 1871, 326. Jahr. Chem. 1871, **24**, 1030, N. Arch ph. Nat **40**, 277.

[12] Compt. rend. 1871, **73**, 114; Zts. Chem. 1871, **14**, 348; Bull. Soc. Chim. 1871, **16**, 301; Jahr. Chem 1871, **24**, 417; Dingl. Poly. 1871, **202**, 374; Chem. News, 1871, **24**, 141; Bull. Soc. Franc. Phot. 1873, **19**, 204; J. C. S. 1871, **24**, 811. L. Leygue and P. Champion, Compt. rend. 1871, **73**, 1478; Mon Sci. 1872, **14**, 79; Dingl. Poly. 1872, **203**, 303; Chem. Centr. 1872, **43**, 75; Wag. Jahr. 1872, **18**, 300.

[13] Dingl. Poly. 1873, **207**, 473. Compt. rend. 1875, **81**, 982; Jahr.

In 1872 appeared the disclosures of Kleffel,[2] H. Mussen,[3] S. Mackie,[4] and the inaugural essay of C. Mitchell[5] on guncotton and its preparation. Mitchell tried a number of experiments with a view of ascertaining the relative proportions of cotton and acids and the proper time for maceration, necessary to obtain a nitrocotton of highest yield and solubility, with maximum explosive power. The following formula was finally adopted: Purified cotton, 7 av. oz.; HNO_3, sp. gr. 1.42, 4 parts; H_2SO_4, sp. gr. 1.84, 4 parts at a temperature of 50°–70° F. In this year the work of J. Lauer on "compressed guncotton" was published in Vienna. E. Nicholson and A. Price[6] proposed to indicate the gradual deterioration of guncotton by impregnation with traces of litmus

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Chem 1875, **28,** 1076, Chem Centr 1876, **47,** 8 Bull Soc Chim 1875, **24,** 439, Amer. Chemist, 1876, 232, Mon Sci 1876, **18,** 193 Wag Jahr 1876, **22,** 480, J C S. 1876, **29,** 516 Compt rend 1876, **83,** 707, Wag Jahr 1881, **27,** 339, Chem. Tech Rep 1876, **15,** I, 388; Chem Centr 1876, **47,** 739, Wag Jahr. 1877, **23,** 479, Bull Soc Franc Phot 1877, **23,** 78, Dingl Poly 1877, **224,** 345, Compt rend 1877, **83,** 77, **84,** 609, Jahr. Chem 1877, **30,** 1159, J C S 1877, **31,** 304, Chem Centr 1877, **48,** 323, Compt rend 1877, **84,** 609 See also H Pellet, Mon Sci 1878, **20,** 558, Chem Ind 1878, **1,** 337; Wag Jahr 1878, **24,** 450, Chem Tech Rep. 1878, **17,** II, 186

[1] Pogg Ann 1871, **144,** 310, Jahr Chem 1871, **23,** 1122 Amer Chemist, 1872, **2,** 345, J C S 1872, **25,** 337 Poly. Centr 1872, **38,** 191

[2] Les Mondes, Jan 18, 1872, Amer Chemist, 1872, **2,** 434 Charzal, Bull de la Soc Franc de Phot 1878, **24,** 31

[3] Dingl Poly 1872, **204,** 510, Zeit Ver Deut Ing. **16,** 255

[4] E P 2693, 1872, 445, 1873, 4230, 1880; F P 99589, 1872, abst. J. A C S 1882, **4,** 41, Wag Jahr. 1881, **27,** 330, Ber 1874, **7,** 742; Dingl Poly. 1874, **213,** 174, Bayr. Ind Gewerbebl 1874, 276; Chem Tech Mitth 1874–1875, 218. S. Mackie and C Faure, E P. 1830, 1873 S. Mackie, C. Faure and G. Trench, E P. 2062, 3612, 1874; 2742, 1876, 198, 1877.

[5] Amer. J. Pharm. 1872, **44,** 241; Chem Tech Rep. 1872, **11,** I, 159; Mon. Phot 1872, **11,** 181; Pharm J Trans. (3), **2,** 1047; Jahr Chem. 1872, **25,** 984; Chem. Centr. 1872, **43,** 554; J C S 1873, **26,** 540. Mon Phot. 1873, **12,** 30; Phot Archiv. 1873, 12; Poly. Centr 1873, **39,** 593; Poly. Notiz 1873, No. 6; Chem. Tech. Mitth. 1872–1873, 49. Bull. Soc. Franc. Phot. 1874, **20,** 119; Chem. Tech. Rep. 1875, **14,** II, 217

[6] E. P. 2430, 1871; abst. Ber. 1872, **5,** 441, abst. Wag. Jahr. 1872, **18,** 299, Deut. Indztg. 1872, **10,** 238; Chem. Tech. Rep. 1872, **11,** I, 129.

or ultramarine, and periodically examining the products for development of acidity from the color of the indicator. E. Brown[1] found that nitrocellulose containing 20% of water does not explode. M. Berthelot made the first of his numerous contributions on the energy of explosive substances in 1871,[2] the author discussing the subject, especially from the thermodynamic standpoint. His conclusions were that guncotton, unlike nitroglycerol, does not contain sufficient oxygen for its complete combustion, the products formed on explosion, therefore, being exceedingly complex. It differs from other explosive substances rather by greater initial pressure than by maximum work, the empirical results of Piobert[3] agreeing well with the calculated result. Whereas theory shows the desirability of causing guncotton to explode in the minimum space, as practiced by Abel in compressing it (see p. 2160). He found that more energy may be obtained from guncotton by adding to it niter or potassium chlorate, but as the combustion is then complete, the effects of dissociation during the expansion of the products are less evident, and the mixture will have greater bursting power.

In a later communication, Berthelot found that when guncotton is prepared by the action of nitro-sulfuric acid, the reaction being interrupted at the end of 20 minutes and the product weighed in order to determine the amount of acid fixed, it was each time found to amount to 4.5 equivalents. 11,000 heat units were disengaged per equivalent of acid fixed, or 55,000 in the normal reaction:

$$C_{12}H_{20}O_{10}\ 5HNO_3C_{12}H_{15}O_5(NO_2)_5\ 5H_2O$$

These numbers, compared with nitroglycerol, explain the relatively greater stability of guncotton. The amount of heat liberated in the explosive decomposition of nitroglycerol, calculated on the most probable hypothesis, is about double that evolved by an equal weight of guncotton.

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[1] Dingl Poly. 1872, **206**, 500; Mechanics Mag. 1872, 478; Poly. Centr. 1873, **39**, 268; Deut. Industrieztg 1873, 38; Wag. Jahr. 1873, **19**, 355; Chem. Tech. Rep. 1873, **12**, I, 150. F. Kreke, Arch. Neerland, **7**, Jahr. Chem., 1872, 155.

[2] Compt rend. 1871, **73**, 260; J. C. S. 1871, **24**, 873; Jahr. Chem. 1871, **24**, 80; Bull. Soc. Chim. 1871, **16**, 223; Chem. Zts. 1871, **14**, 345; Mon. Sci. 1871, **13**, 40-57; Ann. Chim. Phys. 1871, **23**, 223; Chem. Centr. 1872, **43**, 81; Chem. News, 1872, **25**, 166. Ann. Chim. Phys. 1891, **23**, 503; Compt. rend. 1891, **112**, 16; abst. Jahr. Chem. 1891, **44**, 222. See also Compt. rend. 1856, **42**, 1111; Institut. 1856, 205; Arch. ph. nat. **32**, 333; J. prakt. Chem. 1856, **69**, 450; Chem. Centr. 1856, **27**, 625; Jahr. Chem. 1856, **9**, 662.

[3] "Traite d'Artillerie," partie theoretique, 496. L. Peck, Pop. Sci. Month. 1879, **14**, 696.

In 1873 appeared the contributions of Ferrier,[1] Guilleminot,[2] J. Lovering,[3] Carett,[4] and Reygondaud,[5] and the improvements in guncotton manufacture of Burkart.[6] The latter found that guncotton ignited in thin wooden boxes, burns without explosion; but if the walls are thicker than 1/2 inch, explosion ensues. R. Radau[7] determined, in a repetition of the experiments of Berthelot mentioned above, that one kilo of guncotton in exploding, exerts a force equivalent to 172 metric tons. A. Biennait[8] patented a cartridge waterproofed by collodion, while Spooner and the Pyroxyline Manufacturing Co.[9] advocated admixing cotton with the fibers of Esculapius weed or flax, previous to nitration, to obtain special effects.

The next year witnessed the comparatively unimportant developments of A. Chardon,[10] Liebert,[11] Courvoisier[12] and Cassan,[13] and the patented processes of C. Carobbi and G. Bellini,[14] for an explosive material for actuating an air compressing engine, and made of nitrated rags, of C. Faure and G. Trench[15] for an explosive of guncotton, charcoal, barium nitrate and potassium chlorate, and of L. de Froideville[16] for collodion-coated cartridges and torpedoes.

[1] Mon Phot. 1873, **12,** 169, Bull. Soc Franc Phot. 1873, **19,** 292
[2] Mon. Phot. 1873, **12,** 57; Bull. Soc Franc Phot 1873, **19,** 94, 1875, **21,** 87 Mon. Phot. 1875, **14,** 58.
[3] Pop. Sci. Monthly, 1873, **2,** 61.
[4] Mon. Phot. 1873, **12,** 41; Bull. Soc. Franc Phot. 1873, **19,** 60.
[5] Mon. Phot. 1874, **13,** 129.
[6] Berggeist, 1872, 507, 523, 537, 547, 614; Poly Centr 1872, **38,** 1482; 1873, **39,** 131; Jahr Chem 1873, **26,** 1027, Dingl Poly. 1873, **207,** 173.
[7] Mon. Sci. 1873, **15,** 835; Wag. Jahr. 1873, **19,** 354. Jahr Chem. 1873, **26,** 1030.
[8] E. P. 1348, 1873.
[9] E. P. 1170, 1873.
[10] Bull. Soc. Franc. Phot. 1874, **20,** 91. Monit. Phot. 1877, **16,** 117.
[11] Bull. Soc. Franc. Phot. 1874, **20,** 162
[12] F. P. 96530, 1874; abst. Bull. Soc. Chim., 1874, **21,** 192; Wag. Jahr. 1874, **20,** 425.
[13] Monit. Phot. 1874, **13,** 105. Bull Soc Franc. Phot 1874, **20,** 169, 287. See also G. Brown, Poly. Centr. 1874, **40,** 67.
[14] E. P. 961, 1874.
[15] E. P. 3781, 1874; abst. Ber. 1876, **9,** 649; Dingl. Poly. 1876, **221,** 94; Deut. Ind. Ztg. 1876, 228; Wag. Jahr. 1876, **22,** 479; Chem. Tech. Rep. 1876, **15,** I, 388; Bayer. Ind. u. Gewerbebl. **8,** 141; Chem. Tech. Mitth. 1876, **26,** 206; Zts. Chem. Grossgewerbe, 1876, **1,** 233.
[16] E. P. 1275, 1874

The communications of D. Bickford,[1] H. Beins,[2] F. Dumas,[3] Gripon,[4] Greening,[5] the Vigorite guncotton explosive, of O. Nordenfeldt and E. Bjorkman,[6] and the xyloidine fuse of D. Spill.[7]

O. Lohse[8] reported examination of the light spectrum of exploding guncotton, and described definite lines and wave lengths, but H. Vogel showed that the spectrum was due to traces of calcium present as an unavoidable impurity in the nitrated cellulose.[9] Billaud and Ballaudof[10] made minor contributions.

The year 1876 is conspicuous for the paucity of meritorious contributions. Carbutt,[11] H. Grimes,[12] and the nitrocellulose explosive of J. Bantock,[13] and the nitrated wood pulp of E. Gardner[14] may be cited.

The year following, Bolton,[15] G. Canet,[16] H. Eales,[17] C. Klie,[18] E. Kirchner,[19] and F. Hess and J. Schwab,[20] illuminated various

[1] E P. 1170. 1873, abst Ber 1875, **8,** 171, Wag. Jahr 1875, **21,** 532; Chem Tech Rep 1875, **14,** I, 217, Chem News, 1874, **29,** 74

[2] Pop Sci Mon 1875, **7,** 247. See also G Wakely, Wilson's Phot Mosaics, 1875, 30.

[3] Bull Soc. Franc Phot. 1875, **21,** 5

[4] La Nature, 1875, 570

[5] E P. 2044, 1875, F. P 110571, 1875, abst Mon Sci 1876, **18,** 1095

[6] E Bjorkman, E P. 2459, 1875, abst. Chem Tech Mitth 1877, **27,** 340, Deut. Ind Ztg 1876, 58, Chem Tech. Rep 1875, **14,** II, 216, Zts Chem Grossgewerbe, 1876, **1,** 233 See also Dingl Poly 1877, **225,** 108, Jahr Chem 1877, **30,** 1160, Berg u Huttenm Ztg **38,** 123

[7] E P 1739, 1875, abst Ber 1876, **9,** 226, Wag Jahr 1877, **23,** 384.

[8] Pogg Ann 1873, **150,** 641, Jahr Chem 1873, **26,** 151, Chem Centr 1874, **45,** 113, J C S. 1875, **28,** 119

[9] Dingl Poly 1878, **229,** 101, Wied Ann Phys 1878, **3,** 615, Jahr Chem. 1878, **31,** 170, Zts Chem Grossgewerbe. 1878, **3,** 680

[10] Bellaudof, Bull. Soc Franc. Phot 1874, **20,** 47. Also spelled "Billot and Billaudot," Bull Soc Franc. Phot 1877, **23,** 121 See also, J. Gavey, Chem Tech Rep 1878, I, 355. F. Homann, Ann 1878, **190,** 282, J. C. S. 1878, **34,** 399.

[11] Bull Soc Franc Phot. 1876, **22,** 94

[12] Wilson's Photographic Mosaics, 1876, 80

[13] E. P 4806, 1876

[14] E. P 3056, 1876

[15] Phot Mitth 1877, **14,** 197

[16] Rev d'Artil 1877, **9,** 375

[17] D. R P 1853, 1877; abst Chem Ind 1878, **1,** 275, Chem Tech. Mitth. 1878–1879, **28,** 295; Chem. Tech. Rep. 1878, **17,** I, 256.

[18] Proc. Amer Pharm Assoc. 1877, **25,** 286; Amer. J. Pharm 1877, 301

[19] Chem Tech. Rep. 1877, **16,** I, 400. Muencke (D R P. 690, 1877; abst. Wag. Jahr. 1878, **24,** 466, 467; Chem. Ind. 1878, **1,** 127) saturated nitrocellulose with paraffin or other easily fusible indifferent substance to water proof it.

[20] Wien. Acad Ber 1877, **75,** II, 702; Jahr. Chem 1877, **30,** 524. F. Hess, Mitth. Gegen. Artil Genie-Wesens. 1878, 121; abst. Wag Jahr. 1878, **24,** 461; Dingl. Poly. 1878, **229,** 484; J. A. C. S. 1879, **1,** 366; Zts. anal. Chem. 1879, **18,** 352; Rev. d'Artil. 1879, **13,** 339, 540. Mitth. Gegen. Artil. Genie-

angles of the subject, while W. Goddefroy[1] published his method to obtain "guncotton perfectly soluble in ether." S. Davey,[2] and also T. Davey[3] disclosed methods for the co-nitration of starch and sugar in the formation of commercial explosive preparations.

As judged by the memoirs published, a diminution of interest was manifested in 1878, the more meritorious contributions upon nitrated carbohydrates including the publications of C. Beckerhinn,[4] de Pietteurs,[5] A. Ford,[6] Heemkerch,[7] E. Judson,[8] and the relatively important disclosures of M. v. Forster[9] and of G. Wolfram.[10] The former compressed guncotton in a small tube, and used as a detonator, the work of the latter author is taken up in connection with the topic "Chemistry of the Cellulose Nitrates (p. 1614).

In 1879 may be recorded the work of Cooper,[11] A Daubree,[12] Harrison,[13] the guncotton and barium nitrate mixture of J. Hutter,[14]

Wesens 1880, pt V, Chem Tech Rep 1880, **19,** I, 339, Mitt Lab des Tech u Administativen Militaer Committe 1880, Wag Jahr 1880, **26,** 372, Proc U S Nav Inst 1881, **7,** 198

[1] Proc Amer Pharm Assoc 1877, **25,** 285; Zts Oesterr Apoth Ver 1877, 709, Yr Book Pharm 1877, 241, Chem Tech Rep 1877, **16,** I, 538, Amer J Pharm 1877, **49,** 374

[2] E P 2832, 1877, abst Ber 1878, **11,** 1390, Chem Centr 1878, **49,** 640, Wag Jahr 1878, **24,** 467, Chem Tech Rep 1878, **17,** I, 355, Dingl Poly 1877, **230,** 188, Chem Ind 1878, **1,** 108 F. P. 126339, 1879, abst Mon Sci 1879, **21,** 1029

[3] E P 2072, 1860, abst Poly Centr 1860, **31,** 476, Dingl Poly 1860, **156,** 78, Jahr Chem 1860, **13,** 694

[4] Rev d'Artil 1878, **11,** 481

[5] Bull Soc Franc de Phot 1878, **24,** 256

[6] E P 2002, 1878, abst J A C S 1879, **1,** 301

[7] D R P 5144, 1878, abst Dingl Poly 1879, **233,** 349, Chem Tech Rep 1879, **18,** II, 221

[8] D R P 6064, 1878, Dingl Poly 1879, **234,** 253, Chem Tech Rep. 1879, **18,** I, 290, Wag Jahr 1879, **25,** 423, Chem Ztg 1879, **3,** 96, J A C S 1879, **1,** 303, Zts Chem Grossgewerbe, 1879, **4,** 286

[9] Chem Tech Rep 1880, **19,** I, 341 D R P. 10816, 1879, abst Dingl Poly 1880, **238,** 328 Ecl Engin **31,** 113, **35,** 381, Berg Huttenmann. Ztg. 1878, 117, Wag Jahr 1880, **26,** 378, Industriebl. 1880, 438

[10] Dingl Poly 1878, **230,** 45, 148; J C S 1879, **36,** 218, Chem Centr. 1878, **49,** 792, Jahr Chem 1878, **31,** 923, Wag Jahr 1878, **24,** 449, Pharm. Centralh 1879, **20,** 13, Proc Amer Pharm Assoc 1879, **27,** 437, Chem. Tech Rep 1878, II, **17,** 188

[11] Bull. Soc Franc Phot. 1879, **25,** 9

[12] Rev. d'Artil 1879, **15,** 93.

[13] Bull Soc Franc. Phot. 1879, **25,** 283

[14] D. R. P. 3867, 1878, abst. Ber. 1879, **12,** 208, J A C. S. 1879, **1,** 120; Industrieztg. 1879, 121; Ber 1879, **12,** 208; Chem. Ind. 1879, **2,** 50; Chem. Ztg 1879, **3,** 96; Berg. u. Huttenm. Ztg 1879, 175, Dingl. Poly 1879, **232,** 188; Chem. Centr. 1879, **50,** 448; Wag. Jahr. 1879, **25,** 423; Zts. Chem. Grossgewerbe, 1879, **4,** 287, Chem. Tech. Rep. 1879, **18,** I, 290.

the celloidin of E. Schering,[1] the lead nitrate and nitrocotton combination of L. O'Shea and C. Brooks,[2] the pyroxylin lacquer of H. Parkes with camphor and carbon tetrachloride as solvent[3] and the communications of L. Warnecke[4] and Bardy.[5]

It was in 1879 that the first of a series of unusually important papers appeared by E. Sarrau and P. Vieille,[6] on the decomposition of guncotton in closed vessels, the pulverulent guncotton used in the experiments having the composition C, 24; N, 12.7; O, 55.6; H. 2.4; residue, 2.4; and moisture, 2.6. Measurements of the pressures produced by deflagrating different quantities in a cylinder capable of holding 30.3 cc. gave the following results:

Density of Products	Pressure in Kilos per Sq. Cm.	Density of Products	Pressure in Kilos per Sq. Cm.
0.10	1,190	0.30	5,920
0.15	2,200	0.35	7,730
0.20	3,090	0.45	9,760
0.25	4,670	0.55	11,840

The heat produced by the combustion of one kilogram of the dry substance = 1,045 cals., the density of the products being 0.023 under a pressure of 250 kilos. The volume of permanent gas measured at 0° and 760 mm. produced by 1 kilogram of the dry substance varied with the density of the products.

Density	Volume of Gas
0.010	658.5 liters
0.023	669.1 liters
0.200	678.7 liters

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[1] E. P. 1451, 1877; 4771, 1879; D. R. P. 2660, 1878; abst. J. A. C. S. 1879, **1**, 175, 179; Dingl. Poly. 1879, **231**, 94; **232**, 192; Ber. 1879, **12**, 310; Deut. Industrieztg. 1879, 18; Chem. Ind. 1879, **2**, 85; Wag. Jahr. 1879, **25**, 420; Chem. Tech. Rep. 1878, **17**, II, 166; 1879, **18**, I, 233; Industriebl. 1879, 94; Phot. Corresp. **16**, 134.

[2] E. P. 4394, 1879.

[3] E. P. 1869, 1879; D. R. P. 10210, 1879; abst. J. A. C. S. 1880, **2**, 231; Dingl. Poly. 1880, **238**, 262; Wag. Jahr. 1880, **26**, 835.

[4] Phot. Mitth. No. 177, 239; abst. Chem. Ztg. 1879, **3**, 198; Chem. Tech. Rep. 1879, **18**, I, 288.

[5] Bull. Soc. Franc. Phot. 1879, **25**, 46.

[6] Compt. rend. 1879, **89**, 165, 169; 1880, **90**, 1058, 1112; abst. Chem. News, 1879, **40**, 89; 1880, **41**, 273, 282; **42**, 282; J. A. C. S. 1879, **1**, 399; 1880, **2**, 435; J. C. S. 1880, **38**, 780; 1881, **40**, 342, 483; Bull. Soc. Chim. 1880, **33**, 581; **34**, 556; Mon. Sci. 1879, **21**, 958; 1880, **22**, 680, 686; Rev. Sci. 1879, **24**, 117; Ber. 1879, **12**, 2157; 1880, **13**, 1369, 1477; Chem. Centr. 1880, **51**, 391; Chem. Ind. 1879, **2**, 322; Chem. Tech. Rep. 1879, **18**, II, 218; Dingl. Poly. 1879, **233**, 494; 1880, **237**, 253; Jahr. reine Chem. 1880, **8**, 31; Jahr. Chem. 1879, **32**, 1116; 1880, **33**, 127, 1303, 1304; Wag. Jahr. 1879, **25**, 419; 1880, **26**, 380. Compt. rend. 1881, **93**, 269; abst. Jahr. Chem. 1881, **34**, 1131; Chem. News, 1879, **40**, 89.

The average composition of the gas also varied in a similar manner.

Density	Pressure	CO_2	CO	H	N
0 023	250	23 72	43 24	17 28	15 76
0 200	3090	28 68	37.61	18 95	14.85
0 300	5020	30 42	36 28	18.76	14.54

No methane, hydrocyanic acid, nor nitrous vapors were formed. The amount of water produced in the experiments under the lowest pressure was equal to 15.6% of the weight of the guncotton employed. In all the experiments, with the exception of the determinations of the pressures, the guncotton was deflagrated in an atmosphere of nitrogen. When deflagrated in oxygen, the results are somewhat modified.

In a second memoir[1] it was determined that guncotton, under ordinary pressures, when detonation does not occur, but the substance is simply inflamed by a fuse, the products of the decomposition are very different. The following table gives the composition of the gas produced by the combustion of 1 kilo of different explosives:

	NO	CO	CO_2	H	N	CH_4	Total Liters
Guncotton .. .	139	237	104	45	33	7	565
Guncotton with 50% potassium nitrate .	71	58	57	3	7	0	196
Guncotton, with 60% ammonium nitrate . .	122	65	103	12	112	0	414
Nitroglycerol	218	162	58	7	6	1	452

In every case nitric oxide and carbonic oxide are produced in considerable quantities. It is, therefore, necessary in mining operations, to take special care to ensure detonation.

In a third contribution,[2] upon the heat of formation of guncotton, these authors studied the decomposition of ordinary guncotton, $3C_6H_7(NO_2)_3O_5 — C_6H_8(NO_2)_2O_5$, under various conditions, and find that at pressures near that of the atmosphere the whole of the nitrogen is eliminated as nitric oxide, but at higher pressures it is reduced, and the sole products of combustion are nitrogen, hydrogen, carbonic oxide and anhydride, and water, the proportion of carbonic oxide and water decreasing with increase of pressure, while that of the carbonic anhydride and hydrogen increases. The heat of combustion of guncotton was found to

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1. Compt. rend. 1880, **90**, 1058, 1112; abst. J. C. S. 1880, **38**, 780; Ber. 1880, **13**, 1477; Bull. Soc. Chim. 1880, **33**, 581.
2. Bull. Soc. Chim. 1880, **33**, 581; abst. J. C. S. 1881, **40**, 342.

be 1070 cals. per kilogram, and the heat of formation 542 per kilogram, or 620 per equivalent.

They found[1] that the heat developed by the decomposition of an explosive is a quantity of the first importance in calculating theoretically the maximum amount of work which it can do. The actual determination of this quantity is, however, a matter of difficulty, since the nature of the decomposition depends on the conditions under which it takes place, and consequently the amount of heat developed also varies. If, however, the heat of formation of the compound, and the composition and heat of formation of the products of decomposition are known, the heat developed by the decomposition can be calculated, for it will be equal to the excess of the heat of formation of the products above that of the original compound. In order to determine the heat of formation, it is necessary to know the actual heat developed by the combustion of the substance, the composition of the products, and their heats of formation. The heat of formation of the explosive is equal to the difference between the heat of formation of the products of the combustion and the heat developed by the combustion. In order to entirely convert the explosive into simple products, and thus avoid the errors due to incomplete combustion, the authors burn the explosive in an excess of oxygen, and determine the amount of heat developed, and the volume and composition of the gases produced. In this way they have determined the heat of formation of the principal explosives, with the following results:

Nitroglycerol. Heat of formation 94.0 cals. The number calculated from the heat of combustion of glycerol as determined by Louguinine, and the heat of formation of nitric acid and its action on glycerol as determined by Berthelot is 96.0 cals.

Nitro-mannitol. Heat of formation, 161.5 cals.

Guncotton. $C_{24}H_{29}N_{11}O_{42}$. Heat of formation, 639.5 cals.

In 1880, may be noted the developments made by W. Wahl,[2] R. Warren,[3] A. Moreau,[4] H. Trotman.[5] The blasting and mining cartridge of F. Hurd[1] comprized wet guncotton fired electrically; J. Engels described "Atlas dynamite,"[2] H. Prod'homme[3] combined nitrocotton with the nitrates of potassium, sodium, calcium and barium, while J. Lanfrey and J. Renard[4] put upon the market an explosive made by nitrating straw, which is said to be able to absorb 75% of nitroglycerol.

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[1] Compt. rend. 1881, **93**, 213, 269, abst. J. C. S. 1881, **40**, 968; J. C. S. 1881, **40**, 1033. See also Rev. Sci. 1881, **28**, 190, 221. Proc U. S Nav. Inst. 1882, **8**, 306; Jahr. Chem. 1881, **34**, 1151; Jahr. Wag. 1881, **27**, 341; Chem. Ind. 1881, **4**, 384; Chem. Tech. Rep. 1881, **20**, II, 134.

[2] Pop. Sci. Monthly, 1880, **16**, 859.

[3] U. S. P. 227601, 1880; abst J. A. C. S. 1880, **2**, 229.

[4] Proc. U. S. Nav. Inst. 1881, **7**, 483; Mem. Soc. Ing. Civils., Dec.,

In the period up to and including 1880, appeared a number of contributions to various phases of the nitrocellulose art, of which at least, mention should be made in a historical survey of the subject. These included the writings of Caron,[5] Oppermann,[6] Lutrand,[7] W. Brande,[8] J. Stenhouse,[9] J. Russel,[10] E. Schultze,[11] A. Sobrero,[12] Sauerwein,[13] J. Persoz,[14] Hislop,[15] v. Buda,[16] Melland,[17]

1880, Schools of Mines Quart **3,** No 2 Proc U S Nav. Inst 1881, **7,** 497, Rev d'Artil, Nov 1881 Proc U S Nav Inst 1881, **7,** 499, Mem Soc Ing Civils, Sept 1881

[5] E P 2536, 1879, abst Ber 1880, **13,** 1149, J A C S 1880, **2,** 300, Chem Ind 1880, **3,** 205, Chem Tech Rep 1880, **19,** 340

[1] E P 3474, 1880

[2] D R P 10232, 1879, abst Dingl Poly 1880, **238,** 328, 332, Chem. Ztg 1880, **4,** 522, 723, Wag Jahr 1886, **32,** 319, 1887, **33,** 575; Jahr. Chem 1888, **41,** 1311, J A C S 1880, **2,** 105, Chem Ind 1880, **3,** 276, Industriebl. 1880, 339, Chem Tech Rep 1880, **19,** I, 339 See also Deut. Ind Ztg 1880, 401

[3] E P 4200, 1880, abst Wag Jahr 1881, **27,** 331, J A. C. S. 1882, **4,** 48, Chem Ind 1881, **4,** 99, 180, 304, Ber 1881, **14,** 2319, Jahr reine Chem 1881, **9,** 136, Chem Tech Rep 1881, **20,** II, 135

[4] D R P 12115, 1880, abst J A C S 1881, **3,** 76; Bull Soc. Chim. 1881, **35,** 287, Chem Ind 1881, **4,** 55, Chem Tech Rep 1881, **20,** I, 148; Dingl Poly 1881, **240,** 34, Tech Chem Jahr 1881, **4,** 115, Wag Jahr 1881, **27,** 331, Industriebl 1881, 95 E P 3119, 1878, abst Dingl Poly. 1879, **234,** 253, Chem Ztg 1879, **3,** 463, Industriebl 1879, 275, Wag. Jahr. 1879, **25,** 418, J A C S 1879, **1,** 405, Chem Tech Rep 1879, **18,** I, 289, Chem. Ind 1878, **1,** 350 F P 124789, abst Mon Sci 1879, **21,** 1037, 1049 U S P 276833 Belg P 49853 Aust P. 5524 Ital P. Aug. 17, 1878. Port P June 11, 1879 Swed P Aug 20, 1880

[5] Cosmos, **6,** 146, abst Poly Centr 1855, **21,** 632, Jahr. Chem. 1855, **8,** 181

[6] Zts Arch u Ing Ver 1861, **7,** 264, Bayer Kunst u Gewerbebl 1862, 526, Wag Jahr 1861, **7,** 517, 1862, **8,** 280, Poly Centr 1861, **27,** 1553; 1862, **28,** 221; Dingl Poly 1861, **162,** 187

[7] J Pharm Chim 1850, **18,** 428

[8] Pharm J Trans **6,** 388

[9] Roy Soc Trans 1848, **138,** 76, 1849, **139,** 399, J prakt Chem. 1864, **92,** 332, Ann 1848, **68,** 78, 1849, **70,** 226, 1864, **130,** 302, abst. Jahr. Chem. 1849, **2,** 460, 466, Chem Centr 1849, **20,** 625, 627, Chem Gaz. 1849, 265; Phil Mag 1849, **34,** 463, Instit. 1849, 268 See also J. C. S. 1863, **16,** 399; 1864, **17,** 299, abst Chem Centr 1864, **35,** 47.

[10] Les Mondes, 1865, **7,** 737, Mechanics Mag. **12,** 106; J. Sci. **1,** 401.

[11] "Das Neue Chemische Schiesspulver," Berlin, 1865, 35. Wag. Jahr. 1864, **10,** 245, 251; Dingl Poly 1864, **174,** 323, Berg. u. Hüttenm. Ztg. 1864, 348.

[12] Ann. 1845, **64,** 397, Jahr. Chem. 1847-1848, **1,** 1145; Amer. J. Sci.

Pannier,[1] Bizio,[2] Pohl,[3] C. Weber,[4] D'Almeida[5] as well as others.[6]

Fluxation of the Art, Period 1881–1890. The general, broad theoretical aspects of the chemistry of the cellulose nitrates were

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1847, **4**, 274; Compt. rend. 1847, **24**, 247; **25**, 121; Dingl. Poly. 1847, **105**, 387; Ann. Rep. Chem. 1847–1848, **2**, 377; J. prakt. Chem. 1847, **40**, 421; Berz. Jahr. 1849, **28**, 358; Rev. d'Artil. 1877, **9**, 297.

[13] Mitth. Hanover. Gewerbeverein. 1861, 302; Dingl. Poly. 1862, **164**, 123; Proc. Amer. Pharm. Assoc. 1862, **11**, 144; Poly. Centr. 1862, **28**, 459; Wag. Jahr. 1861, **7**, 234; 1862, **8**, 280; Chem. Centr. 1862, **33**, 865.

[14] Poly. Centr. 1866, **32**, 198, 617. Deut. Ind. Ztg. 1867, 5; Wieck's Gewerbeztg. 1867, 96; Chem. Centr. 1867, **38**, 448; Wag. Jahr. 1867, **13**, 564; J. Soc. Arts, 1867, **15**, 19.

[15] Phot. Jahr. **1**, 75. Brit. J. Phot. **17**, 75.

[16] Phot. Jahr. **14**, 128; Brit. J. Phot. 1900, **47**, 128.

[17] Mech. Mag. N. S. **15**, 227.

[1] Mon. Ind. Belg. **6**, 252.

[2] L'Instit. No. 709, 251.

[3] Poly. Centr. 1848, **14**, 1534.

[4] J. S. C. I. 1893, **12**, 117; abst. Chem Ztg. Rep. 1893, **17**, 85.

[5] J. de Physique, 1913, (5), II, 121

[6] Amat. Photo. 1893, **17**, 361; 1898, **28**, 866; Am. J. Pharm. 1860, **32**, 449; Ann. 1861, **119**, 111, 112; Am. J. Photo 1862, **5**, 23; Anthony Photo. Bull. 1890, **21**, 616; Arch. Pharm. **154**, 270; abst. Poly. Centr. 1861, 747; Bayerisches Industrie und Gewerbe-Blatt, 1870, **2**, 216; Chem. News, 1860, **1**, 208; 1861, **4**, 41; 1862, **5**, 140; 1863, **7**, 180; **8**, 141, 175; 1864, **9**, 25', 268, 284; **10**, 102, 161, 296; 1865, **12**, 278; 1866, **14**, 250; 1867, **15**, 10, 47, 189; **16**, 222; 1870, **22**, 263; 1909, **99**, 83, 136, 152, 159; Chem News, Amer. Reprint, 1867, 274; Chem. Tech. Rep 1869, **8**, I, 103; 1871, **10**, II, 100; 1872, **11**, I, 129; 1891, **30**, I, 186; Chem. Centr. 1849, 207, 307; Ding Poly J. 1846, **102**, 252, 331, 408; 1847, **103**, 42, 48, 53, 209, 224; 1863, **169**, 77; 1872, **203**, 325; Wehr. Ztg. 1882, 13; Deutsche Heeres Ztg. 1882, 17; Engng **4**, 467; N. Erfind. u. Erfahr. 1880, **7**, 538; Harpers Weekly, 1909, **53**, 33, Berg. u. Huttenmann Ztg. 1867, 48; Ind. Ztg. **20**, 171; Ind. Bl **26**, 17; J. Soc Arts, **12**, 357, 686; Jahr. Phot. 1898, **12**, 404; 1902, **16**, 515; 1905, **19**, 423; 1914, **28**, 75; J. Frank. Inst. 1881, **78**, 141; J. C. S. 1864, **16**, 2; 1868, **20**, 326, 333; J. prakt Chem. 1847, **40**, 193, 413; **41**, 242; 1848, **43**, 42, 242; **45**, 375; Mon. Phot. 1863–1864, **3**, 36; 1865–1866, **5**, 4, 138; 1866–1867, **6**, 9, 87, 96; 1867–1868, **7**, 30, 78; 1870–1871, **10**, 134, 135; 1874, **13**, 105, 127; La Nature, 1875, I, 254; Militär-Wochenblatt, Nov. 1846, No. 48; Mechanic's Magazine, **27**, 47; Deut. Industrieztg. **10**, 56; Les Mondes, 1865, **7**, 464; 1865, **9**, 510; 1874, **33**, 243; 1878, **47**, 641; N. Erfind. u. Erfahr. 1876, **3**, 338; 1879, **6**, 91, 92; 1881, **8**, 281; 1897, **24**, 126; Poudre Coton, 1868, **24**, 1133; 1870, **28**, 54; Photo. Mitth. **4**, 233; Photo. 1897, **9**, 624; Pharm. Centr. 1903, **45**, 302; N. Report f. Pharm. 1872, **1**, 6; Pharm. Ztg. 1891, 113; Am. J. Pharm. 1872, **44**, 165; 1891, **63**, 189; Gewerbebl. Würtenberg, 1864, **14**; Pr. Mech. J. **8**, 172, 201; **9**, 253, 286, 314; Poly. Centr. 1847, **13**, 36, 161, 416, 1533; 1848, **14**, 1532; 1849, **15**, 1464; 1854, **20**, 1468; 1855, **21**, 1471; 1861, **27**, 746; 1863, **29**, 1171; 1869, **35**, 1193; Pharm. J. Trans. **5**, 273; **6**, 207, 264, 938; **7**, 478; **8**, 421; **9**, 84, 487; **15**, 430; Romb. Ztg. **39**, 54; Rev. d'Art. **33**, 171; Sci. Amer. 1881, **45**, 58; Soc. Can. 1881, **9**, 162; Engng. 1881, **32**, 535; Sci. Am. **61**, 25447; 1882, 5099; 1887, 223; Wag. Jahr. 1864, **10**, 238, 239, 245, 246; 1869, **15**, 268; 1871, **17**, 318; 1878, **24**, 117; Glückauf, 1879, 8; Wieck's Gewerbeztg. 1867, 410; Witthaus Med. Chem. 1881, 312; Waffenschm. **2**, 91; Chem. Tech. Mitth. 1861–1862, 46; 1863–1864, 150; Chem. News, Amer. Reprint, 1869, **4**, 97; Weavers Military Explosives, 1912. Jahr. Chem. 1847–1848, **1**, 1143; 1849, **2**, 471. See also Mellez, J. Pharm. Chim. 1851, **20**, 128.

pretty clearly elucidated during this decade, as indicated in the topic "Chemistry of the Cellulose Nitrates," and coupled with the exact knowledge on stability and decomposition which resulted from the laboratory and mental analyses of previous investigators, this period is remarkable for the number and diversity of commercial ramifications of the art as a whole. Pharmacy, photography, lacquers, plastics--all seemed to receive an impetus in this period, not so much from investigations chronicled from 1881 onward, as from the economical fruition of past investigations apparently dormant.

In the development of thermoplastic pyroxylin combinations, may be noted the processes of C. Lockwood,[1] S. Hoggson and G. Pettis,[2] G. Dean,[3] L. Beals,[4] I. Drummond,[5] and the explosive products of C. Bjorkman,[6] J. Lewin,[7] and S. Mackie,[8] which are fairly representative of tendencies in this direction. The collodion photographic emulsion of J. Wolfram,[9] the cellulose nitration processes of M. Sanlaville and S. Roche,[10] Pochez and Piquet,[11] together with the contributions of E. Price-Edwards,[12] T. Laidley,[13] J. Eder,[14]

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1. U S. P 246891, 1881, abst J A C S 1881, **3**, 166.

2 U. S P 245952, 1881, abst. J A C S 1881, **3**, 164

3. U. S. P. 241941, 1881; abst. J A. C. S. 1881, **3**, 159

4 U S P 239423, 239424, 239425, 1881, abst J A C. S 1881, **3**, 68.

5 U S P 248413, 1881, abst J A C S 1881, **3**, 168

6 E P 2483, 1880, abst Wag Jahr 1881, **27**, 330; J A C S. 1882, **4**, 41, Chem Ind 1881, **4**, 65, 207, Ber 1881, **14**, 1426, Poly Notizbl 1881, **36**, 398, Jahr reine Chem 1881, **9**, 136, Chem Tech Rep 1881, **20**, II, 136; J. S C I 1882, **1**, 382

7. U S. P. 242783, 1881; D R. P 15073, 1881; abst. J A C S 1881, **3**, 161; 1882, **4**, 80, Dingl Poly 1882, **246**, 184, Wag Jahr. 1881, **27**, 330; J A C. S. 1882, **4**, 80, Chem. Ind 1881, **4**, 281, 326, 358, Ber 1881, **14**, 2433, Jahr Chem. 1881, **34**, 1274, 1882, **35**, 1411, Industriebl 1881, 343, Chem Tech Rep 1881, **20**, II, 135, J S. C I 1882, **1**, 31

8. E. P. 4230, 1880; abst Wag Jahr 1881, **27**, 330, J A. C S 1882, **4**, 41, Chem Ind 1881, **4**, 99, 180, 223, Ber. 1881, **14**, 1426, Chem Tech Rep. 1881, **20**, I, 149.

9. D. R. P 12266; abst. Wag. Jahr 1881, **27**, 904.

10. D. R. P. 14619; abst. Chem. Ind 1881, **4**, 358, Indbl. 1881, 351; Chem. Tech. Rep. 1881, **20**, II, 135; Wag Jahr 1881, **27**, 331, J S C I. 1882, **1**, 31; Bull Soc Chim. 1883, **39**, 364.

11. F. P. 146181, 1881; abst Mon Sci 1882, **24**, 734.

12 Pop. Sci. Month. 1881, **19**, 428.

13. U. S. Serv. M. 1881, **1**, 345

14. J. Eder, Sitzungsber. K. Akad der Wissensch 1879, **129**, Mar.; abst. Wag. Jahr. 1879, **25**, 390; Chem. Ind 1880, **7**, 246; Wien. Acad. (2 Abt.), **79**, 537; Jahr. Chem. 1879, **32**, 833, J prakt. Chem. 1879, (2), **19**, 294; J. C. S. 1879, **36**, A, 911; Year Book of Pharm. 1880, 80; Phot. Corr. 1879, **16**, 67; Sci. Amer. Suppl. 1880, 3777. Ber 1880, **13**, 169; Dingl. Poly. 1880, **237**, 253; Amer. J. Sci. 1880, (3), **19**, 405; J. A. C. S. 1880, **2**, 173; Zts. ang. Chem. 1881, **20**, 135; Jahr. Chem. 1880, **33**, 1005; Sci. Amer. Suppl.

A. Brown,[1] Van der Bogaert,[2] W. Boehler[3] and C. Munroe,[4] indicate advancement in the year 1881. To the foregoing should be added the comparatively unimportant disclosures of T. Witherbee,[5] and nitrocellulose-nitroglycerol explosives of J. Anders.[6]

In 1882 appeared the colloiding process of guncotton by superficial treatment with methyl or ethyl alcohol;[7] the F. Katschinsky method of collodion cotton manufacture;[8] and the communications of A. Ford,[9] J. Lefevre[10] and M. Berthelot and P. Vieille.[11]

The next year G. McRoberts published his notes on blasting gelatin,[12] F. Petry disclosed a method of explosive paper formation,[13]

1880, 3777, Chem Ind 1880, **7,** 246; Sitz. Ber. Wien. Akad. **79,** II, 537; Tech Bl **12,** 173, 216; Phot Corr **16,** 117; Phot Mitth. **16,** 97; Phot. News, **25,** 149; Bull Soc Franc Phot. 1881, **27,** 119, Chem Tech. Rep. 1880, **19,** II, 338; Dingl Poly 1881, **239,** 475; Wag. Jahr. 1881, **27,** 899. J. C. S. 1882, **42,** 111.

[1] Pop Sci Mon 1882, **21,** 773 See also J. and J. Moller, D. R. P. 24772, abst Chem Tech, Rep. 1883, **22,** II, 156.

[2] Rev. d'Artil 1881, **18,** 488 493.

[3] Proc. U S. Nav. Inst 1881, **7,** 473.

[4] Proc U. S Nav Inst. 1879, **5,** 21.

[5] Proc U. S. Nav. Inst. 1882, **8,** 298; School of Mines Quart. (3), **4,** 296; Engineer, Dec 2, 1881

[6] E P. 800, 801, 1881; abst J. A. C. S. 1882, **4,** 48, Wag. Jahr. 1881, **27,** 331; Chem Ind 1881, **4,** 140, 384; Ber. 1881, **14,** 2318; Jahr. reine Chem. 1881, **9,** 136, Chem Tech Rep. 1881, **20,** II, 136. His preparation, which was known as Diaspongelatine, consisting of a mixture of nitrated wood fiber, nitroglycerol and sulfur.

[7] W. Reid, D. R. P. 18950, 1882; abst. Dingl. Poly. 1882, **246,** 46. J S C. I. 1911, **30,** 851; abst. C. A. 1911, **5,** 3341. W. Reid and D. Johnson, E. P. 619, 1882, Aust. P. April 24, 1883; abst Wag. Jahr. 1883, **29,** 389; Dingl. Poly. 1883, **248,** 509, Chem. Tech. Rep. 1883, **22,** I, 202; Chem. Ind. 1883, **6,** 10.

[8] Russ Zts Pharm **21,** 795, abst Jahr. Chem. 1882, **35,** 1473; Chem. Centr. 1882, **53,** 9; Apoth. Ztg. 1882, **3,** 583.

[9] Rept H M Insp. Exp. 1882, **45,** No. 28, 1883, **55,** Sept. 19; 1899, 145, abst J. S. C. I 1899, **18,** 415.

[10] Rev d'Artil. 1882, **20,** 88.

[11] Ann Chim. Phys 1880, **21,** 564; Chem. Ind 1882, **4,** 88; Compt. rend 1880, **90,** 946; Bull Soc. Chim. 1881, **35,** 599; Chem. Tech. Rep. 1882, **21,** II, 176. P Vieille, Compt. rend. 1882, **95,** 132; abst. Wag. Jahr. 1882, **28,** 1013.

[12] Proc. Phil Soc. Glasgow, April **25,** 1883; abst. Proc. U. S. Nav. Inst. 1885, **11,** 94, J. S. C. I. 1890, **9,** 265, 476; Zts. ang. Chem. 1890, **3,** 492; Wag Jahr. 1890, **36,** 541; Chem. Ztg. 1890, **14,** 379; Chem. Tech Rep. 1890, **29,** I, 225; II, 146; Jahr. Chem. 1890, **43,** 2705, 2708; Tech. Chem. Jahr. 1890–1891, **13,** 156, 161, 171; Dingl. Poly. 1890, **278,** 418; Mon. Sci. 1891, **37,** 391; Bull. Soc. Chim. 1891, **6,** 518, 521; Rev. Chim. Ind. 1891, **2,** 267; Chem. Ind. 1891, **14,** 74.

[13] Boston J. Chem. 1875, **9,** 112; abst. Proc. U. S. Nav. Inst. 1885, **11,** 115. D. R. P. 21160; abst. Chem. Tech. Rep. 1883, **22,** I, 202; Wag. Jahr. 1883, **29,** 389; Chem. Ind. 1883, **6,** 27, 52; Ber. 1883, **16,** 265; Poly. Notiz. 1884, **39,** 120; Chem. Tech. Jahr. 1882–1883, **5,** 176.

while the G. Wolf process of pyroxylin manufacture was detailed.[1] It was in this year that the extensive experiments in the compression of guncotton were communicated by M. von Forster,[2] and in conjunction with W. Wolf[3] the development of a colloid nitrocotton powder which is made commercially to this day. The xylonite process of J. Edson,[4] and the disclosures of M. Hasse & Co.,[5] J. Bergerou,[6] J. Cundill,[7] W. Siemens,[8] W. Springer,[9] and J. Spiller,[10] indicate the developmental tendencies.

E. Nolting and A. Collin detailed their extensive experiments of nitrating under diverse conditions in 1884,[11] and W McClintock the velocities produced by Schultze and E. C. powder in small arms.[12] Similar is the work of A. Gaudin,[13] H. Abbot[14] and C. Curtis.[15] The spontaneous decomposition of explosive gelatin

[1] Pharm Zts Russ 1883, 4, abst Amer J Pharm 1883, **55,** 273, Proc Amer Pharm Assoc 1883, **31,** 242

[2] Berg u Huttenm Ztg 1878, 117, Dingl Poly 1878, **228,** 284, Zts Chem Grossgewerbe, 1878, **3,** 380 Dingl Poly 1883, **250,** 466, abst J S C I 1884, **3,** 329 Van Nostrand's Mag 1884, **31,** 113, abst Proc U S Nav Inst 1885, **11,** 109, Chem News, 1885, **52,** 185, Dingl Poly 1884, **251,** 371, Jahr Chem 1884, **37,** 1750, Chem. Ind 1884, **7,** 133, Chem Ztg 1884, **8,** 348, Chem Tech Rep 1884, **23,** I, 200, J C S 1884, **46,** 948, J S C. I 1884, **3,** 330, Industriebl 1884, **21,** 165 Chem Ztg 1886, **10,** 530, abst Chem Tech Rep 1886, **25,** I, 158 Dingl Poly 1886, **261,** 25, abst Jahr Chem 1886, **39,** 2077, J S C I 1886, **5,** 502, Wag Jahr 1886, **32,** 324, Chem Tech Rep 1886, **25,** II, 296 Proc U S Nav Inst 1886, **12,** 563, 1889, **15,** 373, 513; Dingl Poly 1888, **269,** 240, Pop Sci Mon 1888, **32,** 133 See also Dingl Poly 1880, **238,** 328

[3] D R P 23808, abst Wag Jahr 1883, **29,** 389, Dingl Poly. 1885, **256,** 408, Chem Ind 1883, **6,** 250, 348; Ber 1883, **16,** 2542, Chem Tech Rep 1883, **22,** II, 188. D. R P. 26014, abst Wag Jahr 1884, **30,** 377; Chem Ind 1884, **7,** 31, 165; Chem. Tech Rep 1884, **23,** I, 201, Bull Soc Chim. 1884, **42,** 398; Poly. Notizbl. 1884, **39,** 187 See also Dingl Poly. 1883, **250,** 456, 1884, **251,** 371

[4] D. R. P. 28296, 1883, abst Dingl Poly 1884, **254,** 231, Wag Jahr. 1884, **30,** 1204.

[5] D. R. P. 24903, 1883; abst. Dingl. Poly. 1884, **252,** 152, Tech Chem. Jahr. 1883-1884, **6,** 166

[6] Pop. Sci. Mon. 1883, **22,** 495.

[7] Rep. H. M. Insp. Exp Mar. 10, 1883, Rep No 49

[8] Wag. Jahr. 1883, **29,** 391.

[9] E. P. 1445, 1882, abst. Chem. Ind 1883, **6,** 6, Wag Jahr 1882, **28,** 1008; J S C I. 1882, **1,** 163; Chem. Tech Rep 1883, **22,** I, 155.

[10] Monit Phot 1883, **22,** 152. Phot News, 1883, **27,** 453

[11] Ber. 1884, **17,** 261; abst. J. A. C. S. 1884, **6,** 309, J. C S. 1884, **23,** 1011; J S. C I. 1885, **4,** 399; Jahr. Chem. 1884, **37,** 660.

[12] Proc. Roy. Artil Inst 1883, **12,** 332, Proc U S Nav. Inst. 1884, **10,** 221. See also Rev. d'Artil. 1885, **26,** 599

[13] Rev. d'Artil. 1884, **25,** 189; Armee Blatt, No 37. See also Amer J Sci 1888, **36,** 48.

[14] Eng. and Min. J. 1884, **37,** 26, Wag Jahr 1884, **30,** 381, Dingl. Poly 1884, **252,** 152. See also Wag. Jahr. 1883, **29,** 399.

[15] Eng. Min. J. 1883, **36,** 366; abst. Dingl. Poly. 1884, **252,** 154.

engaged the attention of C. Munroe,[1] and patents were issued to Pile,[2] and J. Schulhof[3] for guncotton explosives. T. Nordenfelt and V. Meurling[4] disclosed their method for hydrocellulose nitration, and G. Mowbray[5] evolved a plastic of pyroxylin and mica.

F. Gilles described the nitration of molasses in 1885,[6] in which year Mankowsky[7] pointed out quantitatively the influence of traces of sulfuric acid in combination, as affecting the stability of nitrocotton. W. Mixter[8] demonstrated that pure guncotton shows the same reducing property to Fehling's solution as the lower cellulose nitrates, but approximately half as much copper oxide is formed as with pyroxylin. R. Penniman and J. Schrader[9] patented a "gelatinated" nitroglycerol and ammonium nitrate powder; and G. Balagny,[10] and also A. Bechamp[11] engaged themselves with new methods of cellulose nitrate manufacture.

The next year contributions were, speaking generally, of minor importance. They included the patented processes of M. Lindsley[12] and also M. Bielefeld[13] for nitrocellulose explosive compounds, the plastic combinations of J. Jarvis[1] and the dynamite mixture of M. Eissler.[2] P. Dudley[3] reported on new methods of molding guncotton, K. Rohrer[4] on nitrocotton especially suitable as filling for shells, while T. Jewett,[5] M. v. Wendland,[6] Laukmamer,[7] and C. Hilt,[8] disclosed minor points.

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[1] Proc. U. S. Nav. Inst. 1884, **10,** 220 J A. C S 1884, **6,** 13, abst Dingl. Poly. 1884, **252,** 156; Wag. Jahr. 1884, **30,** 372, Chem Ind 1884, **7,** 165; Chem. News, 1884, **49,** 259; Chem. Tech. Rep. 1884, **23,** I, 201, J. C. S. 1884, **46,** 947; Jahr. Chem. 1884, **37,** 1748.

[2] Phot. Corres. 1884, **21,** 222.

[3] U. S. P. 304361, 1884; abst. J A. C. S. 1884, **6,** 314 J. Schulhof, E. P. 4917, 1882; abst. Wag. Jahr. 1884, **30,** 377; Chem. Ind. 1883, **6,** 375, Ber. 1883, **16,** 2941; Jahr. Chem. 1883, **36,** 1705, Pharm. Rundschau, 1883, 759; Chem. Tech. Rep. 1883, **22,** I, 201, II, 190; Poly Notizbl 1884, **39,** 76.

[4] D. R. P. 30676, 1884, abst. Dingl Poly. 1885, **255,** 337, 340, Proc. U S. Nav. Inst. 1886, **12,** 195. Wag. Jahr. 1885, **31,** 279; J. S. C. I. 1885, **4,** 366; Jahr. Chem. 1885, **38,** 2102; Ber. 1885, **18,** 130-R, Chem Ind 1885, **8,** 66, 144.

[5] U. S. P. 294661, 1884; 349659, 350498, 1886, 443105, 1890; abst. J. A. C. S 1884, **6,** 145, 1886, **8,** 238, 239, 1890, **12,** 507.

[6] D. R P 27969; E. P 1883, 1883, abst. Ber. 1884, **17,** 455-R, Dingl. Poly. 1885, **255,** 337; abst J. C. S. 1885, **48,** 852; Proc. U S. Nav. Inst. 1886, **12,** 195, Jahr. Chem. 1885, **38,** 2102, J S. C I. 1884, **3,** 35; 1885, **4,** 366; Chem. Ind. 1884, **7,** 355, Wag. Jahr. 1884, **30,** 379, Tech. Chem. Jahr. 1883–1884, **6,** 173; 1888, **11,** 185.

[7] Bull. Soc. Chim. 1885, (2), **43,** 124; abst. Jahr. Chem. 1885, **38,** 2197.

[8] Amer. Chem. J. 1891, **13,** 507; abst. Jahr. Chem. 1891, **44,** 808, 1323. See also Ann. Chim. Phys. 1843, (3), **8,** 233. Jahr. Chem. 1885, **38,** 1173.

[9] U. S. P. 333151, 1885; abst. J. A. C. S. 1886, **8,** 29.

[10] Belg. P. 68346, 1885.

[11] Bull. Soc. Franc. Phot. 1885, **1,** II, 228; see also A. Bechamp, Compt. rend. 1885, **100,** 117, 279; Jahr. Chem 1885, **38,** 340; J. C. S. 1885, **48,** 237; Ber. 1885, **18,** 113, 141; Bull. Soc. Chim. 1885, **43,** 661; Chem. News, 1884, **50,** 300; 1885, **51,** 142.

[12] U. S. P. 333872, 1886; abst. J. A. C. S. 1886, **8,** 30; Chem. Ztg. Rep. 1886, **10,** 121; Chem. Tech. Rep. 1886, **25,** I, 254.

[13] U. S. P. 340276, 1886; abst. J. A. C. S. 1886, **8,** 112.

In 1887 J. Graydon[9] gave an exhaustive résumé of the employment in Germany of guncotton for charging projectiles, which was amplified by D. Johnson,[10] and M. Dumas-Guilin.[11] It was in this year that F. Crane[12] brought forth his modern pyroxylin-resin lacquer process, and the propulsive powders of E. Schultze,[13] H. Schoeneweg,[14] and E. Du Pont were granted patent protection.[15] G. Darwin[16] read a paper on the use of guncotton to produce artificial earthquakes (in the past they had been produced unintentionally), C. Stocker[17] brought forward his "unburnable collodion," and Blacher,[18] and also Chevreau,[19] added their *grain* to the sum total of our knowledge in this field.

C. Munroe[20] contributed observations on the theory of action of cocoa powder; and the wave-like effects produced by detonating guncotton.[1]

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[1] U. S. P. 342208, 1886, abst. J. A. C. S. 1886, **8,** 159.

[2] U. S. P. 347421, 1886, abst. J. A. C. S. 1886, **8,** 236, Chem. Tech. Rep. 1886, **25,** II, 298, Wag. Jahr 1886, **32,** 319, J. A. C. S. 1886, **8,** 236.

[3] Pop. Sci. Mon. 1886, **29,** 433, 605.

[4] Proc. U. S. Nav. Inst. 1886, **12,** 563, 1889, **15,** 463, Sci. Amer. 1889, 116.

[5] Pop. Sci. Monthly, 1886, **28,** 138, Pop. Miscellany.

[6] D. R. P. 36718, 1886, abst. Ber. 1886, **19,** 721; Dingl. Poly. 1887, **263,** 148, Wag. Jahr 1886, **32,** 322; Chem. Ind. 1886, **9,** 269, 361, Industriebl. 1887, 31; Chem. Tech. Rep. 1886, **25,** II, 297, Ber. 1886, **19,** 721-R.

[7] Waffanschm. 1888, **21,** 160.

[8] Rec. Univ. des Mines, 1885, abst. Rev. Sci. 1886, **37,** 350; Chem. Centr. 1886, **57,** 621; Jahr. Chem. 1886, **39,** 2079; Rec. Univ. des Mines, 1886, **19,** No. 2, abst. Chem. News, 1886, **54,** 24.

[9] Rev. D'Artil. 1887, **30,** 530, Proc. U. S. Naval Inst. 1887, **13,** 413.

[10] Aust.-Hung. P. 2387, 1887; abst. Dingl. Poly. 1888, **267,** 370; Proc. U. S. Nav. Inst. 1890, **16,** 49. Maissin (F. P. 190073, 1888) patented the employment of nitrocotton in grains to form a fuse capable of transmitting fire or detonation to a great distance at the rate of several miles per second.

[11] Proc. U. S. Nav. Inst. 1888, **14,** 773.

[12] E. P. 8253, 15771, 1887, abst. Proc. U. S. Nav. Inst. 1889, **15,** 213, 498; J. S. C. I. 1888, **7,** 363, 443, 882, 1889, **8,** 204.

[13] A. and N. J. 1887, **28,** 673; Proc. U. S. Nav. Inst. 1887, **13,** 593.

[14] Gen. Inform. Ser. 1888, **7,** 375; Proc. U. S. Nav. Inst. 1888, **14,** 759. H. Schoeneweg, U. S. P. 371376, 1887; abst. J. A. C. S. 1887, **9,** 180.

[15] U. S. P. 352611, 1886; 363887, 1887; 590931, 1897; Re. 11651, 1898; abst. Proc. U. S. Nav. Inst. 1887, **13,** 582, 584, 586; Dingl. Poly. 1887, **263,** 149; J. A. C. S. 1886, **8,** 242; Tech. Chem. Jahr. 1887-1888, **10,** 194.

[16] Fortnightly Review, Pop. Sci. Mon. 1887, **31,** 359.

[17] E. P. 16330, 1887; abst. Proc. U. S. Nav. Inst. 1890, **16,** 54.

[18] Pharm. Rund. 1887, 493; abst. Chem. Tech. Rep. 1887, **26,** I, 270.

[19] Industriebl. 1887, 237; J. de Pharm. 1887, (5), **15,** 556, abst. Chem. Tech. Rep. 1887, **26,** I, 192.

[20] Amer. J. Sci. 1884, **6,** 13, 586. Amer. Assoc. Adv. Sci. Aug. 1887;

In 1885 H. Maxim[2] was granted the first of a series of patents for smokeless powder production; H. v. Vessel[3] published analyses of gelatin dynamite and Rhexite, N. Kalakoutski[4] described the existing German smokeless powders; H. Piffard[5] a guncotton and magnesium photographic flash light; and P. Chalon[6] on the action of nitrocotton on metal plates. The celluloidine of E. Turpin[7] was accorded patent protection, and H. Halford[8] and A. Orr[9] made minor contributions. Combinations of picric acid with "tetranitrocellulose" was described by Deutsche Sprengstoff-A. G.[10] and the important patents of H. de Chardonnet for nitrocellulose artificial silk formation[11] were issued, his previous patents being in many ways commercially impracticable. The C. Hengst "im-

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Sci. Amer. 1887, **57,** 223, Proc U S Nav Inst 1887, **13,** 586, 594

[1] Amer J Sci 1888, **36,** (3), 48, Proc U. S. Nav Inst 1888, **14,** 772 See also Pop Sci Monthly, 1888, **32,** 287 J. A C. S 1893, **15,** 1, J A. C. S 1896, **18,** 819, U S Nav Inst 1909, **35,** 715 8th Inter Cong Chem. Appl 1912, C. A. 1912, **6,** 3525.

[2] U S. P 411127, abst Proc U S Nav Inst 1890, **16,** 47; Tech. Chem Jahr 1889, **12,** 160 U S P 430212, abst J A C S 1890, **12,** 240 Tech Chem. Jahr. 1890-91, **13,** 164 U. S P 434049, abst J A C S. 1890, **12,** 359. U S. P 436898, abst J. A. C S 1890, **12,** 365 U. S P 454281, abst. J A. C. S. 1891, **13,** 188. U S P. 544924, abst Chem Ztg 1895, **19,** 1633. D. R. P 49154, abst Zts. ang. Chem 1890, **3,** 59, Jahr Chem 1890, **43,** 2708, Chem. Tech Rep 1889, **28,** II, 173, Wag Jahr 1889, **35,** 475, Ber. 1890, **23,** 42-R; Industriebl 1890, 87, Tech Chem Jahr. 1889, **12,** 160

[3] Mitt Art Genie Wessen, 1887, 565, Dingl Poly. 1888, **267,** 473, **268,** 523.

[4] Rev d'Artil 1888, **33,** 171, 179, 1889, **34,** 76, 579; Revista Artigliera, 1889, No 2, 7, 8; A and J. No 1299; Oesterr. Ung. Wehr. Ztg. No 62.

[5] Proc U. S Nav. Inst. 1888, **14,** 443, Newport News, Oct. 31, 1887.

[6] Le Genie Civil, Proc. U S Naval Inst 1888, **14,** 773.

[7] E. P. 4310, 1888, F P 189398, 1888, abst. Proc U. S. Nav. Inst. 1889, **15,** 312; J. S. C I. 1889, **8,** 61; Mon Sci. 1888, **32,** 1262

[8] A. and N. J. 1888, **25,** 601, Proc U S Naval Inst 1888, **14,** 439.

[9] E P. 487, 1888; abst. Proc. U. S Nav Inst. 1889, **15,** 213; J. S. C. I. 1889, **8,** 204.

[10] D. R P 42452, 1887; abst Dingl Poly 1888, **268,** 516; Chem. Tech. Rep. 1888, **27,** I, 165, Chem. Ind. 1888, **11,** 441; Wag. Jahr. 1888, **34,** 491; Ber. 1888, **21,** 334-R, Mon. Sci. 1888, **32,** 1332, Tech. Chem. Jahr. 1887–1888, **10,** 191; Zts. ang Chem. 1888, **1,** 150

[11] U. S. P. 455245, E P 5270, 1888; abst. J. A. C S 1891, **13,** 189; J. S. C. I 1889, **8,** 474; J Soc Dyers Col. 1889, **5,** 151 D R. P. 64031; abst. Zts. ang. Chem. 1892, **5,** 499; Chem. Centr. 1892, **63,** II, 1088, Chem. Ztg. 1892, **16,** 1432; 1893, **17,** 1004; Chem. Tech Rep 1892, **31,** II, 164; Chem. Ind. 1892, **15,** 485, Wag. Jahr. 1892, **38,** 376, Ber. 1892, **25,** 892-R; Mon. Sci. 1892, **40,** 166; Industriebl. 1892, 358, Meyer Jahr. Chem. 1892, **2,** 362; Tech. Chem. Jahr. 1892–1893, **15,** 169, Proc U. S Nav. Inst. 1888, **14,** 443; Sci. Amer Suppl. 1888, **25,** 10, 230. See also Compt rend. 1907, **145,** 115; abst. J. S. C. I. 1907, **26,** 892.

proved safety smokeless gunpowder" was patented in 1888.[1]

The year 1889 did not witness any especially noteworthy contributions to this subject. The development of blasting gelatin and "bellite" was detailed by J. Kerr,[2] J. Skoglund[3] disclosed the formula for the nitrocellulose powder "grakrult;" C. Lamm,[4] G. Mach[5] and F. Gaens[6] contributed. The colloidal cellulose of C. Guignet[7] was developed in this year.

The explosive of C. Lundholm[8] and with J. Sayers;[9] of D. Mendeleff[10] of pyroxylin, nitroglycerol and methyl or ethyl nitrates; and of W. Schuckher,[11] J. Longridge,[12] and the gelatinous smokeless powder of F. Abel,[13] to which tannin was added to impart a propulsive character, were disclosed in 1890. The process of J. France[14] for the nitration of powdered cotton issued in this year.

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[1] This was made of nitrated oat straw E P 13656, 1888, abst. Proc U S Nav Inst 1889, **15,** 497, J S C I 1889, **8,** 478, 1890, **9,** 325, Zts ang Chem 1890, **3,** 247, Wag Jahr 1890, **36,** 546, Chem Ztg 1890, **14,** 408, Chem Tech Rep 1890, **29,** I, 222, Tech Chem Jahr 1889, **12,** 165, Jahr Chem 1890, **43,** 2710 D R P 48265, abst Zts ang Chem 1889, **2,** 1266, Jahr Chem 1889, **42,** 2863, Chem Tech Rep 1889, **28,** I, 183, Chem Ind 1889, **12,** 416, Wag Jahr 1889, **35,** 473, Ber 1889, **22,** 525-R

[2] Proc U S Nav Inst 1889, **15,** 297, J S C I 1889, **8,** 213 Glasgow Herald, March 6, 1889

[3] E P 18362, 1888, abst Proc U S Nav Inst 1889, **15,** 498, J S C I 1889, **8,** 478, Chem Ind 1889, **12,** 416, Chem Tech Rep 1889, **28,** I, 184 F P 194905, abst Mon Sci 1889, **34,** 756 See also Sci Amer 1889, 312

[4] Rev d'Artil 1890, **36,** 175, 188, 197, 277

[5] Rev d'Artil 1889, **35,** 297, 383, 393, 498

[6] D R P 48933, abst Chem Ind 1889, **12,** 466, Chem Tech Rep 1889, **28,** II, 171, Ber 1889, **22,** 525 R, Tech Chem Jahr 1889, **12,** 163, Zts ang Chem 1889, **2,** 554, Wag Jahr. 1889, **35,** 473. Jahr Chem 1889, **42,** 2682

[7] Compt rend 1889, **108,** 1258, Amer J Sci 1889, (3), **38,** 408, Proc. U. S Naval Inst. 1890, **16,** 53, Chem Tech Rep 1889, **28,** I, 145, Chem. Ztg Rep. 1889, **13,** 194.

[8] E P 10312, 1889, abst Dingl Poly. 1890, **278,** 19, J S C I 1890, **9,** 764, Tech Chem. Jahr 1890, **13,** 160

[9] U S P. 438816, 1890; E P 6399, 1889, abst J A C S, 1890, **12,** 418; Dingl Poly 1890, **278,** 19, J S C I 1890, **9,** 414, Tech Chem Jahr. 1890-1891, **13,** 153

[10] U S P 440921, 1890, abst J A C S 1890, **12,** 478

[11] D R P 51755, abst Indbl 1890, 293, Jahr Chem 1890, **43,** 2710, Chem Ztg 1890, **14,** 739, Chem. Tech Rep 1890, **29,** I, 223, Chem. Ind. 1891, **14,** 36, Wag. Jahr 1890, **36,** 545, Ber 1890, **23,** 528-R, Tech. Chem. Jahr. 1890-1891, **13,** 157.

[12] Rev. d'Artil 1890, **37,** 295

[13] U S. P. 425648, 1890, abst. J A. C S 1890, **12,** 125 F. Abel and J. Dewar, E. P. 11664, 1889, abst Dingl. Poly. 1890, **278,** 19; J. S. C. I. 1890, **9,** 765; Tech. Chem Jahr 1890-1891, **13,** 163

[14] U. S P. 420445, 420446; 1890; abst J. A. C S. 1890, **12,** 22.

A. Hertzog,[1] Britton,[2] R. v. Bieberstein,[3] U. Allason,[4] J. Ducros,[5] and v. Goltz,[6] and the works on nitrocellulose by Wiebe[7] and W. de Heusch[8]—the former containing an extensive bibliography—appeared also during this year.

Cellulose Nitrate Research, Period 1891-1900. During this decade, in taking a survey of the ephemeral and permanent contributions made, ideas advanced and patents perfected, there is no one epoch-making discovery that stands out above the others, to which a distinct impetus has been given to the art. Rather, advancement during this period has been by gradual increment and cumulative effect.

In 1891 appeared the disclosures of R. Schüpphaus,[9] W. Walke,[10] Weiss,[11] Thiel,[12] S. v. Romocki,[13] G. Saunders,[14] I. Lifschütz,[15] Morton-Liebschütz[16] and J. Lifschütz,[17] none of which was of extraordinary importance. The next year O. Mühlhauser,[1] H. Schjerning[2] and O. Witt[3] investigated the "cumulative detonation" of mixtures of wet and dry guncotton. Kruger,[4] C. Munroe[5] and C. Weber,[6] also contributed.

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[1] Centr. Text. Ind. 1890, 975; abst. Chem Tech. Rep 1890, **29**, II, 143.

[2] Deutsche Herr Zeit Aug 27, 1890; J. Roy. U. S Instit. 1891, **34**, 1031.

[3] Rev. d'Artil. 1890, **36**, 283; Colburn's U. S. Mag. Feb 1890.

[4] Rome, Voghera Carlo Review 1889; abst. Rev. d'Artil. 1890, **37**, 90.

[5] Rev. d'Artil. 1890, **37**, 134.

[6] Rev. d'Artil 1890, **36**, 385.

[7] Rev. d'Artil. 1890, **36**, 538

[8] Rev. d'Artil 1890, **36**, 479.

[9] Investigations commenced in 1891, culminated in 1895, J. S. C. I. 1895, **14**, 556

[10] J. A C. S. 1890, **12**, 256; abst. Jahr. Chem. 1891, **44**, 2668, Mon. Sci 1891, **37**, 395.

[11] Pharm Ztg. 1891, 113; abst. Wag. Jahr 1891, **37**, 749. See also Papierztg. **36**, 113; abst. Chem. Centr. 1891, **62**, I, 681.

[12] Mitt. d. Ver. f. Gewerb. Sitzungsb. 1891, 193; Wag Jahr. 1891, **37**, 436; Chem. Tech. Rep. 1891, **30**, II, 254; Pap. Ztg. 1891, 2416; Indl. 1892, 14; Berg. Hütten. Ztg 1892, 23.

[13] D. R. P. 54818; abst Zts ang. Chem. 1891, **4**, 33; Jahr. Chem. 1891, **44**, 2667; Chem. Ztg. 1891, **15**, 80, 1058; 1892, **16**, 1277; Chem. Tech. Rep. 1891, **30**, I, 218; Chem. Ind. 1891, **14**, 98, Wag. Jahr. 1890, **36**, 543; Ber. 1891, **24**, 429-R; Mon. Sci 1891, **37**, 91; Tech. Chem. Jahr. 1890–1891, **13**, 156.

[14] J. Roy. U. S. Inst. 1891, **34**, 867.

[15] I. Lifschutz and Chem Fabr. Grunau, D. R. P. 60233, 69807; abst. Chem. Tech. Rep. 1893, **32**, II, 272; Zts. ang. Chem. 1892, **5**, 154; 1893, **6**, 465; Chem. Centr. 1893, **64**, II, 1015; Jahr. Chem. 1892, **45**, 2899; Chem. Ztg. 1893, **17**, 1213; 1894, **18**, 1089; Wag. Jahr. 1892, **38**, 1020; 1893, **39**, 427; Ber. 1892, **25**, 298; 1893, **26**, 921; Mon. Sci. 1892, **40**, 176; 1893, **42**, 200, 304; 1894, **44**, 56.

[16] Mon. Sci. 1891, (3), **33**, 113; abst. Chem. Centr. 1891, **62**, I, 517; Jahr. Chem. 1891, **44**, 2564; Chem. Ztg. Rep. 1891, **15**, 51; Chem. Tech. Rep. 1891, **30**, I, 218; Zts. anal. Chem. 1891, **30**, 637; Pharm. Centralh. 1891, **33**, 210; Tech. Chem. Jahr. 1890-1891, **13**, 170.

[17] Ber. 1891, **24**, 1186; Jahr. Chem. 1891, **44**, 2811; J. C. S. 1891, **60**, 814; Chem. Centr. 1891, **62**, I, 1055.

The biennial period 1894–1895 disclosed the E. Cramer process for nitrated cellulose filter cloth manufacture,[7] the pyroxylin artificial leather investigations of W. Field,[8] and the work of R. Bader,[9] and of H. Warren.[10] The next year T. Bokorney,[11] Coutagne,[12] Griffith[13] and T. Tyrer,[14] contributed.

The following two years include the publications of the extensive series of researches of Will and Lenz on the nitration of a wide range of carbohydrates,[1] the celluloid patents of Bethisy,[2] the simultaneous comminution and nitration process of A. Liedbeck,[3] the comprehensive résumé of nitrocellulose explosives by M. Merle,[4] the investigations on nitroerythrite by A. Dupre,[5] and the electrical fuse of R. Linke,[6] consisting of a thin platinum wire coated with long fiber nitrated cotton, covered with collodion.

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[1] Dingl Poly 1892, **284,** 137, Wag Jahr 1892, **38,** 374; J. C. S. 1893, **64,** i, 6; Jahr. Chem 1892, **45,** 2732, Chem Centr 1892, **63,** I, 982. See also Dingl Poly. 1864, **173,** 137. Amer. J Pharm. 1892, 144; Chem. Ztg 1892, **16,** 163; Dingl Poly 1892, **283,** 88, 137, Zts ang Chem. 1892, **5,** 196, Proc. Amer. Pharm. Assoc. 1892, **40,** 1004; Chem Tech Rep. 1892, **31,** I, 223.

[2] Zts. anal Chem 1892, **31,** 283; abst J. S C. I 1893, **12,** 62; J. C. S. 1892, **62,** 1520, Zts ang Chem 1892, **5,** 467, Chem Centr. 1892, **63,** II, 425; Jahr. Chem 1892, **45,** 2531; Chem Ztg Rep. 1892, **16,** 243; Wag. Jahr. 1892, **38,** 389; Ber. 1892, **25,** 873-R, Tech. Chem Jahr 1892-1893, **15,** 180; Meyer Jahr Chem. 1892, **2,** 365; Proc Amer. Pharm Assoc. 1893, **41,** 441.

[3] Prom. 1892, **3,** 230

[4] Prom. 1893 **4,** 513

[5] J. A C. S. 1893, **15,** 1. See also Pop Sci. Monthly, 1888, **32,** 287. J. A C. S. 1896, **18,** 819. C. Bunot (E P 5415, 1896) patented pyrotechnic serpentines formed of guncotton and coiled into ribbons

[6] J S. C. I 1893, **12,** 117; abst Zts ang Chem 1893, **6,** 405; Chem. Centr 1893, **64,** I, 758; Jahr. Chem 1893, **46,** 888; Chem Ztg. 1893, **17,** 246, 1004; Chem. Ztg. Rep. 1893, **17,** 86, Chem Tech Rep 1893, **32,** I, 238; Wag. Jahr. 1893, **39,** 428; Ber. 1893, **26,** 327-R, Meyer Jahr. Chem. 1893, **3,** 367; Industriebl. 1893, 158; Tech Chem Jahr 1892-1893, **15,** 171.

[7] Zts. ang. Chem. 1894, **7,** 269, J S C I. 1894, **13,** 833; Proc Amer. Pharm. Assoc. 1895, **43,** 493; Jahr. Chem 1894, **47,** 350.

[8] J. A. C. S. 1893, **15,** 140; 1894, **16,** 487, 543, abst J. S C. I. 1893, **12,** 708; 1895, **14,** 179, 298; Tech Chem Jahr. 1893–1894, **16,** 166; Chem. Centr. 1893, **64,** II, 502; 1894, **65,** II, 541; Bull. Soc. Chim 1894, **12,** 1350; Jahr. Chem. 1894, **47,** 1134.

[9] Chem. Ztg. 1895, **19,** 55, 78; J. C. S 1896, **70,** i, 335; Ber. 1895, **28,** 427 R; Chem. Centr. 1895, **66,** I, 373; Jahr. Chem 1895, **48,** 1297. U. Marga (E. P. 21470, 1895) devized a bullet for practice purposes made of cellulose and nitrocellulose made into a plastic mass with alcohol and ether.

[10] Chem. News, 1895, **71,** 165; abst Jahr. Chem. 1895, **48,** 1360; Chem. Centr. 1895, **66,** I, 1036; Bull. Soc. Chim. 1895, **14,** 914

[11] Pflüger's Archiv. 1896, **64,** 262; J. C. S. 1896, **70,** ii, 869; Chem. Ztg. 1896, **20,** 985; Jahr. Chem. 1896, **49,** 1031; Meyer Jahr. Chem. 1896, **6,** 309.

[12] F. P. 260678, 1896.

[13] Sci. Amer. Suppl. 1896, **42,** 17460.

[14] Pharm. J. 1896, 109; abst. J. S. C. I. 1896, **15,** 672; Ber. 1896, **29,** 1149.

In 1899–1900 appeared the essay of G. Bumcke and R. Wolffenstein[7] on the action of nitrogen peroxide and nitric acid upon cellulose, the analytical scheme of smokeless powder analysis of W. Williams,[8] the investigations on nitrocellulose by A. Luck and C Cross,[9] and the comprehensive work on nitration of cotton by G. Lunge and E. Weintraub.[10]

In the period from 1901 to the present time, development has been so ramified along specialized lines, both in the peaceful and warlike arts, and the increment of knowledge has been so varied, that it, perhaps, may more profitably be touched upon in connection with the elaboration of the individual topics elsewhere herein.

Chemistry of the Cellulose Nitrates. In the preceding historical development of this subject incidental references have been made to the endeavors of the early investigators to elucidate some of the chemical problems in connection with the nitration of cellulose, especially the constitution of the cellulose nitrates, and out of the maze of contradictory and anomalous results attempt to arrive at generalizations founded on exact quantitative determinations.

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[1] Ber 1898, **31,** 68, 81, 87, 89, J C S 1898, **74,** i, 227, J S. C I 1898, **17,** 271, Bull Soc Chim 1898, **20,** 390, Chem Centr 1898, **69,** I, 441; Jahr. Chem. 1898, **51,** 1307; Wag. Jahr 1898, **44,** 707

[2] Bull Soc Franc Phot 1898, II, **14,** 593

[3] D. R. P. 96109; abst Jahr. Chem 1898, **51,** 1382, Wag Jahr. 1898, **44,** 372, Chem Centr 1898, **69,** I, 1222, Mon Sci 1898, **52,** 178, Zts. ang. Chem 1898, **11,** 167. E P 14690, 1897, abst J S. C I 1897, **16,** 760 See also F Liedbeck, E P. 27397, 1898, abst J S C I 1899, **18,** 401

[4] Mon Sci 1897, **49,** 18, abst J S C I 1897, **16,** 934, Jahr. Chem. 1897, **50,** 1062.

[5] Ann Rep H M Insp Expl 1897, 27, J S C I 1899, **18,** 415.

[6] D R. P 92813; abst Wag Jahr 1897, **43,** 484; Chem Centr. 1897, **68,** II, 928; Chem Ztg 1897, **21,** 654

[7] Ber 1899, **32,** 2493, abst J C. S 1899, **76,** i, 852, J. S. C. I. 1899, **18,** 940; Bull. Soc Chim 1900, **24,** 620; Chem Centr. 1899, **70,** 752; Jahr. Chem 1899, **52,** 1290, Meyer Jahr Chem 1899, **9,** 300

[8] J. Frank Inst. 1899, **147,** 197; Wag Jahr. 1899, **45,** I, 425; J. S. C. I. 1899, **18,** 526, Jahr Chem 1899, **52,** 288

[9] J. S C I. 1900, **19,** 642, abst Jahr Chem. 1900, **53,** 848; J. C. S. 1900, **78,** i, 541, Chem Centr 1900, **71,** II, 698, Zts. ang Chem. 1901, **14,** 117, 625; D. R. P. 117349, abst. Wag Jahr 1901, **47,** I, 492; Chem Centr. 1901, **72,** I, 288; Chem. Ztg. 1901, **25,** 93, Zts ang Chem. 1901, **14,** 117; News, Jahr Chem. 1901, **54,** 895; Mon Sci 1901, **57,** 148.

[10] Zts ang Chem 1899, **12,** 441, Chem. Centr 1899, **70,** I, 1177, 1272; J. S C I 1899, **18,** 582, Jahr. Chem. 1899, **52,** 1302. See Chem. News, 1904, **90,** 148.

The earlier chemists who experimented with the nitrocelluloses adopted the formula $C_6H_{10}O_5$ as the simplest expression of the cellulose molecule, and based on the increment of weight which cellulose undergoes upon nitration, assumed that three nitrocelluloses exist, i e., *trinitrocellulose* as the highest obtainable ester and called by them guncotton, a second or intermediary, modification *dinitrocellulose* soluble in ether-alcohol and the product used primarily in photography and in lacquers as a collodion, and a still lower modification *mononitrocellulose*, about which they all agreed, but little definite was known.

According to the "best chemical analysis" of the "most renowned savants of the time," the composition of trinitrocellulose was quite simple, being merely cellulose in which "three atoms of the hydrogen have been replaced by three atoms of hyponitric acid." While it was agreed that assuming the cotton is all converted into the trinitroderivative, 100 parts should yield 185 parts of guncotton, actual experimentation by these "most renowned, etc.," showed a marked lack of unanimity, the following being the results of direct investigation. For every 100 parts of cotton:

		Parts of Guncotton
Pelouze (in ten experiments, 1849)	found	168 to 170
Schmidt and Hecker (1848)	"	169
Van Kerckhoff and Reuter (1849)	"	176 2
W Crum (1850)	"	178
Redtenbacher, Schrotter and Schneider (1861)	"	178
v Lenk (1862)	"	155
Blondeau (1865)	"	165 25

A. Gaudin took "pure" nitrocellulose and separated into *etherzilne* the portion soluble in ether-alcohol, and another fraction which was insoluble, both fractions (naturally) differing in nitrogen content from the original.[1] E. Hadow[2] distinguished the three following products, and detailed careful methods for their preparation:

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[1] Compt rend 1846, **23,** 980, 1100, 1099, abst J prakt. Chem 1847, **40,** 418, Photo. Jahr **17,** 30, Bull de la Soc d'Enc 1847, 65, Berz Jahr. 1849, **28,** 348, 349, Annuaire de Chimie, 1847, **3,** 454

[2] Poly Centr. 1853, **19,** 1471, J C S 1854, **7,** 200, J. prakt Chem. 1855, **64,** 169; Dingl. Poly 1855, **136,** 397, Chem Centr. 1855, **26,**

1. Trinitrocellulose, $C_6H_7(NO_2)_3O_5$, or $C_{18}H_{21}(NO_2)_9O_5$, obtained by immersing cotton in a mixture of 2 molecules fuming nitric acid and 2 molecules 66° Bé. sulfuric acid, and 3 molecules water, the product being insoluble in ether-alcohol, but soluble in ethyl acetate.

2. $C_{18}H_{22}(NO_2)_8O_{15}$, sometimes containing $^1/_2H_2O$, which was more soluble in ether-alcohol than the previously described product, and soluble in glacial acetic acid.

3. $C_{18}H_{23}(NO_2)_7O_{15}$ (xyloidine of Gladstone) formed at first with 1 mol. H_2O, and soluble in ether-alcohol and in glacial acetic acid.

C. Blondeau[1] considered dinitrocellulose as $C_6H_8(NO_2O_5.H_2O)$, which, upon treatment with water, took on an additional 4 molecules of water, and by prolonged action of fuming nitric acid arrived at the ultimate nitration, a cellulose trinitrate. Ransome's formula was inadmissable because it involved the elimination of hydrogen; Pettenkofer's formula was founded on incorrect

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202; Amer. Drug. Circ. **8,** 123; Proc. Amer. Pharm. Assoc. 1864, **12,** 165; Jahr. Chem. 1854, **7,** 625. The existence of three definite compounds of nitric acid with cellulose was admitted by A. Bechamp, who represented their composition as follows. $C_{12}H_{17}(NO_2)_3O_{10}$, $C_{12}H_{16}(NO_2)_4O_{10}$, $C_{12}H_{15}(NO_2)_5O_{10}$; Compt. rend. 1852, **35,** 473; Dingl. Poly. 1852, **126,** 144. Instit. 1852, 318; Chem. Centr. 1852, **23,** 823; Jahr. Chem. 1852, **5,** 658; J. prakt. Chem. 1853, **58,** 15; Ann. Chim. Phys. 1853, (3), **37,** 207. Chim Gaz. Nov. 15, 1852; Amer. J. Pharm. 1853, **25,** 159; J. Pharm. (3), **22,** 440. Chem. Tech. Mitth. 1852–1854, 164. Compt. rend. 1853, **37,** 134; Instit. 1853, 261; J. prakt. Chem. 1853, **60,** 187; Chem. Centr. 1853, **24,** 703; Poly. Centr. 1853, **19,** 687; Jahr. Chem. 1853, **6,** 550; Amer. J. Sci. 1853, (2), **16,** 406; Ann. Chim. Phys. 1856, **46,** 338. Compt. rend. 1855, **41,** 817; Ann. Chim. Phys 1856, **46,** 338; J. prakt. Chem. 1856, **68,** 51; Jahr. Chem. 1855, **8,** 681. Compt. rend. 1856, **42,** 1213; Inst. 1856, 235; Jahr. Chem. 1856, **9,** 674; Ann. 1856, **100,** 367; J. prakt. Chem. 1856, **69,** 449. Compt. rend. 1860, **51,** 257; Zts Chem. Pharm. **3,** 657. Ann. Chim. Phys. 1862, (3), **64,** 311, 322; Chem. Centr. 1862, **33,** 865; 1863, **34,** 690; Wag. Jahr. 1862, **8,** 280; Jahr. Chem. 1862, **15,** 469; 1863, 691; Rep. Chim. Pure, **4,** 358; Bull. Soc. Chim. 1863, **5,** 289; Ann. Chim. Phys. 1855, **44,** 311; 1856, **48,** 458.

[1] Ann. 1863, **118,** 462; Jahr. Chem. 1863, **16,** 567. Compt. rend. 1864, **58,** 1011; J. prakt Chem. 1864, **93,** 318; Jahr. Chem. 1864, **17,** 569; Instit. 1864, 195; Chem. News, 1864, **9,** 286; Chem. Centr. 1865, **36,** 44. Compt. rend. 1865, **59,** 963; Chem. Centr. 1865, **36,** 476; Dingl. Poly. 1865, **178,** 166; Phot. Archiv. 1865 342. Compt. rend. 1865, **61,** 378; Dingl. Poly. 1865, **178,** 147; Chem. Centr. 1865, **36,** 1597; Chem. Tech. Rep. 1865, **4,** I, 116; Wag. Jahr. 1865, **11,** 412; Bull. Soc. Chim. 1865, **13,** 145; Deut. Int. Ztg. 1865, 388; Mon. Sci. 1865, **7,** 898; Inst. 1865, 299; J. prakt. Chem. 1865, **96,** 64.

nitrogen determinations; while R. Porrett's views[1] were characterized as "adventurous."

A. Martin[2] as the culmination of his investigations, came to the conclusion that four different modifications of nitrocellulose exist, differing only in their NO_2 content. W. Grum,[3] in developing the now well known nitrometer, prepared guncotton from Sea Island cotton and obtained a yield of 177.9%, with a nitrogen content of about 0.03% less than the figure given on analysis. His results were unusually accurate and concordant. J. Gladstone[4] found no decomposition in a pure guncotton from nitric acid, sp. gr. 1.5, and concentrated sulfuric acid, which was insoluble in ether, while the nitrocellulose obtained by dissolving cotton in HNO_3 and precipitating with water, developed nitric acid upon standing for some time. To the former he ascribed the formula $C_{24}H_{15}(NO_4)_5O_{20}$, and the latter, $C_{24}H_{17}(NO_4)_3O_{20}$, and considered ordinary guncotton to be a mixture of the two.

A. Bayer[5] studied the decomposition products of the action of phosphorous pentachloride in an endeavor to gain an insight into the structure of the nitric ester molecule. W. Gintl[6] found that pyroxylin is completely decomposed in the cold, and made the statement (which we now believe to be true) that the compounds of nitric acid and cellulose are *esters*. His results are of more than ordinary interest, and stand out as a distinct contribution on the constitution of the cellulose nitrates. By decomposing various cellulose nitrates by means of concentrated sulfuric acid, whereby nitric acid and a substituted sulfuric acid—a lignone sulfuric acid—is formed, he concluded that nitrocellulose "is to be considered as a neutral ester of nitric acid with the complex $C_{12}H_{21}O_{12}$, the latter being an alcohol with three OH groups."

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[1] Phil Mag 1847, (3), **30**, 409, Chem Soc Mem 1848, **3**, 287, J prakt Chem 1847, **41**, 208, Chem Centr 1847, **18**, 689, Jahr Chem. 1847 1848, **1**, 1138

[2] Bull Soc Fran Phot 1861, **7**, 142, Rep Chim Appliq. 1861, **3**, 257, Jahr Chem 1861, **14**, 712

[3] Phil Mag 1847, (3), **30**, 426, J prakt Chem 1847, **41**, 201; J Pharm (3), **12**, 296, Ann 1847, **62**, 233, Jahr Chem 1847-1848, **1**, 1130; Glasgow Phil. Soc Proc 1844 1848, **2**, 163

[4] Chem Soc. Mem 1845 1847, **3**, 412, Pharm j Tran., **11**, 401; **13**, 215; Jahr Chem 1853, **6**, 660, 1863, **16**, 741, Phil Mag 1847, (3), **31**, 519, Chem News, 1863, **8**, 141.

[5] Ber. 1869, **2**, 54, Zts Chem 1869, **12**, 345, Bull Soc Chim 1869, **12**, 292, Jahr Chem 1869, **22**, 742

[6] Wien Akad. Ber. **59**, 809, J prakt Chem 1869, **107**, 478; Zts. Chem 1869, **12**, 703, Jahr Chem 1869, **22**, 753, Poly. Centr 1870, **36**, 159; Chem News, Amer Reprint, 1870, **6**, 115, Bull Soc. Chim. 1870, **13**, 435, Wag. Jahr 1870, **16**, 220; Zts. allg. Oester Apothekerverein 1869, 421, Chem. Tech Rep. 1869, **8**, II, 98, Chem News, 1869, **20**, 323, Proc. Amer. Pharm. Assoc 1870, **18**, 270, 1871, **19**, 261, Pharm. Zts f. Russ. 1870. Nov ; Chem. Centr. 1870, **41**, 159.

G. Wolfram[1] in 1879 communicated the results of a comprehensive series of investigations made with a view of studying the nitro-compounds of various kinds of cellulose, such as cotton, hemp, straw, and also of gelatin, and embodied his conclusions under the following 13 points:

1. By the action of HNO_3 and H_2SO_4 upon cellulose nitro-compounds are formed, which vary with the quantities of the acids, the kind of cellulose, the duration of reaction, and the temperature of the acid mixture.

2. Four nitro-compounds are producible: penta-nitrocellulose, $C_{12}H_5(NO_2)_5O_{10}$; tetranitrocellulose, $C_{12}H_6(NO_2)_4O_{10}$; trinitrocellulose, $C_{12}H_7(NO_2)_3O_{10}$; and dinitrocellulose, $C_{12}H_8(NO_2)_2O_{10}$.

3. Three of these compounds may be obtained in the fibrous and powdered state.

4. The quantity of "hyponitric" (nitric) acid in the nitro-compound increases with the quantity of the sulfuric acid, the concentration of the nitric acid, the duration of the reaction, and the height of the temperature of the acid mixture.

5. Increase of the temperature of the nitrating mixture not only increases the quantity of nitric acid in the product, but also facilitates the penetration of the cellulose, changes its structure, and gives to the pyroxylins and their solutions other physical properties.

6. The products of nitration of cellulose are mostly mixtures of nitrocellulose in various stages of nitration, which, with the exception of the penta-nitrocellulose, are difficult to produce by themselves, and cannot be completely separated by solvents.

7. Nitro-compounds of cellulose containing more than 41.89% NO_2 contain nitric acid in their pores, which cannot be removed

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[1] Dingl. Poly. 1878, **230**, 45, 148; abst. Wag. Jahr. 1878, **24**, 449; Chem. Ind. 1878, **1**, 403; Zts. Chem. Grossgew. 1878, **3**, 860; Jahr. rein Chem. 1878, **6**, 478; J. C. S. 1879, **36**, 218; Chem. Centr. 1878, **49**, 792; Jahr. Chem. 1878, **31**, 923; Chem. Tech. Rep. 1878, **17**, II, 88; Proc. Amer. Pharm. Assoc. 1879, **27**, 437; Ber. 1878, **11**, 2284.

by washing; those containing less than 22.22% NO_2 are mixed with unnitrated cellulose.

8. By a very concentrated nitric and sulfuric acid mixture the various kinds of cellulose are converted into an identical compound; by weaker acid, on the contrary, are nitrated in variable proportions.

9. The more readily the fiber is converted into parchment by sulfuric acid the more difficult it is nitrated, and conversely.

10. Strongly parchmented pyroxylins may be distinguished from those that are not or but little parchmentized, by partial reduction with sulfuric acid solution of ferrous sulfate and coloration with iodine solution.

11. The solubility of the nitrocelluloses differs according to the composition or structure.

12. The production of a glassy layer upon the evaporation of a solution of pyroxylin is not only dependent upon the substance itself, but also on the solvent.

13. By impregnating cotton with gelatin, or by the addition of gelatin to the mixture before nitrating, the conditions for the production of a partly pulverulent pyroxylin may be produced.

A careful contemplation of the above thirteen generalizations in the light of our present day knowledge of the subject, must impress one with the fact that in this investigation of Wolfram are to be discerned many of the embryonic facts upon which the later art has been established. It is now, of course, recognized that there are no definite or distinct stages in cellulose nitration, but that esterification of both normal and modified cellulose apparently proceeds as a continuous process and goes on without a break from 6% up to about 13.5% nitrogen, provided the conditions of esterification are suitable. All attempts up to the present to induce discontinuity in the nitration of cellulose have been unsuccessful.

From analyses made by reduction with ferrous salts, P. Champion and H. Pellet[1] concluded that Abel's compressed guncotton (see p. 1599) consists not of trinitrocelluose, but of pentanitrocellulose; but F. Abel, on the other hand,[1] showed that the analyses upon which their conclusions were founded, were fallacious, inasmuch as no care had been taken to free the guncotton from lower derivatives by extraction with ether-alcohol. Abel found commercial guncotton to consist of about 85% trinitrocellulose with 4%–5% unattacked cellulose, and 10% dinitrocellulose.

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[1] Compt. rend. 1876, **83**, 707; 1877, **84**, 609; Ber. 1877, **10**, 735; Chem Centr. 1876, **47**, 739, 1877, **48**, 323, 739; Wag. Jahr. 1876, **22**, 479; 1877, **23**, 385; 1881, **27**, 339; Chem Tech. Rep. 1876, **15**, I, 388; Jahr. Chem. 1877, **30**, 1159, Jahr reine Chem. 1877, **5**, 175. See also Mon. Sci. 1876, **18**, 1160, Ber. 1876, **9**, 1610, Chem. News, 1876, **34**, 205; Zts. Chem. Grossgew. 1876, **1**, 233.

The Cellulose Nitrates of Eder. In a series of researches published by J. Eder[2] in 1872 to 1880, he carried our knowledge of the chemistry of nitrocellulose a distinct step further in that he described at least four degrees of nitration, and prepared products which at that time were considered well characterized. This necessitated doubling the expressions for the various cellulose nitrates, as Eder required a cellulose molecule of the magnitude $C_{12}H_{20}O_{10}$ to represent the various products he had succeeded in preparing.

Up to this time a number of "nitrocelluloses" had been proposed and formulas deduced, usually from the increase in weight upon nitration and without sufficient regard for the purification by fractional precipitation from solvent combinations, or even approximate separations based upon selective solubility determinations. The chaotic state of this portion of the subject is evidenced from the following formulas for nitrocellulose which had been put forward by previous investigators as follows:

Schönbein and Bottger	$C_9H_{12}N_4O_{13}$
Pelouze	$C_{23}H_{44}O_{17}(N_2O_5)_5$
Schmidt and Hecker	$C_{24}H_{32}O_{21}(NO_2)_{10}$
Peligot	$C_{12}H_{18}O_{12}(NO_2)_6$
v. Kerkhoff and Reuter (called *Typhoxylin*)	$C_{24}H_{26}O_{19}(NO_2)_{12}$
Porret and Teschenmacher[3]	$C_{12}H_{16}O_{10}(NO_2)_4$

[1] Compt. rend 1876, **83,** 1011, Bull Soc Chim 1877, **28,** 28, Chem News, 1877, **35,** 10, abst Ber 1876, **9,** 1939, Wag Jahr. 1877, **23,** 385, Jahr Chem. 1876, **29,** 1111; Mon Sci 1877, **19,** 88, Rev Sci 1876-1877, **18,** 573.

[2] Wien Acad Ber 1879, **129,** 537. Wag Jahr. 1879, **25,** 390, Chem. Ind. 1880, **7,** 246, Jahr Chem 1879, **32,** 833, J. prakt. Chem. 1879, **127,** 294; J. C. S 1879, **36,** 911, Year Book of Pharm 1880, 80, Phot. Corr 1879, **16,** 67; Sci Amer. Suppl. 1880, **7,** 3777 Ber 1880, **13,** 169; Dingl. Poly. 1880, **237,** 253; Amer J Sci 1880, (3), **19,** 405; J A. C S. 1880, **2,** 173; Zts. ang. Chem 1881, **20,** 135, Jahr Chem. 1880, **33,** 1005; Sci. Amer. Suppl. 1880, 3777; Chem. Ind. 1880, **7,** 246 Sitz. Ber. Wien Ak 2 Abth. **79,** 537; Tech. Bl. **12,** 173, 216; Phot. Corr. **16,** 67, 117; Phot Mitth. **16,** 97; Phot. News, **25,** 149; Bull. Sec. Franc Phot. 1881, **27,** 119; Chem. Tech. Rep. 1880, **19,** II, 338.

[3] A collodion pyroxylin soluble in ether-alcohol.

Gladstone, Pelouze and Maurey, Champion and Pellett	$C_{12}H_{15}O_{10}(NO_2)_5$
W. Crum, Gerhardt, Schrotter, Schneider, Redtenbacher, Abel[2]	$C_{12}H_{14}O_{10}(NO_2)_6$
Hadow	$C_{18}H_{21}O_{15}(NO_2)_9$[3]
	$C_{18}H_{22}O_{15}(NO_2)_8$[4]
	$C_{18}H_{23}O_{15}(NO_2)_7$[5]
Fehling	$C_{12}H_{20}O_{14}(N_2O_5)_2$
Ransome	$C_{12}H_{16}O_{10}(N_2O_5)_2$
Bechamp	$C_{12}H_{17}O_{10}(NO_2)_3$[6]
	$C_{12}H_{16}O_{10}(NO_2)_4$[7]
	$C_{12}H_{16}O_{10}(NO_2)_4$[8]
Wolfram	$C_{12}H_{18}O_{10}(NO_2)_2$[9]
	$C_{12}H_{17}O_{10}(NO_2)_3$[10]
	$C_{12}H_{16}O_{10}(NO_2)_4$[11]
	$C_{12}H_{15}O_{10}(NO_2)_5$[12]

In commenting upon the above, Eder truly points out that the results are so contradictory, and the statements of the observers so irreconcilable, as to make accurate generalizations almost impossible. He obtained the following five pyroxylins.

Cellulose hexanitrate	$C_{12}H_{14}O_4(NO_3)_6$	14.14% N.
Cellulose pentanitrate	$C_{12}H_{15}O_5(NO_3)_5$	12.75% N.
Cellulose tetranitrate	$C_{12}H_{16}O_6(NO_3)_4$	11.11% N.
Cellulose trinitrate	$C_{12}H_{17}O_7(NO_3)_3$	9.15% N
Cellulose dinitrate	$C_{12}H_{18}O_8(NO_3)_2$	6.75% N

Whereas up to this time the theory advanced was that by the action of nitric acid on cellulose, two or more hydrogen atoms in the cellulose are displaced by the NO_2 group, and thus *nitro* groups formed, to which the names mono-, di-, and tri-nitrocellulose had been given, it was Eder who first conclusively showed that true nitric esters result in which one or more hydroxyl groups have been displaced by a corresponding number of groups of the nitric acid radical, the terms as above shown being used to designate the various nitric esters of cellulose.

All of the above compounds as prepared by him were decomposed by alkalis with the splitting off of nitrates, he having

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1. A cellulose nitrate insoluble in ether-alcohol Similar to one of the products of Wolfram
2. For guncotton Differs from the preceding by one mol NO_2
3. Insoluble in ether-alcohol and in glacial acetic acid.
4. Soluble in ether-alcohol, but insoluble in glacial acetic acid.
5. Soluble in ether-alcohol and in glacial acetic acid
6. By treatment of collodion with potassium hydroxide
7. By treatment of collodion with ammonia
8. Guncotton, probably insoluble in ether-alcohol.
9. By treatment of collodion with KOH and ammonia.
10. Prepared as the preceding one A constituent of collodion cotton.
11. A constituent of collodion cotton
12. Guncotton, insoluble in ether-alcohol.

determined that the simultaneous production of nitrites is no proof of the existence of the nitro-group. They yield, even in the cold, nearly all their nitrogen in the form of nitrates when treated with sulfuric acid. Towards ferrous sulfate and chloride they behave exactly like other nitrates, reducing agents converting pyroxylin into a modified cellulose free from nitrogen. Hence he deduces that all pyroxylins are constructed after the same general formula:

$$C_{12}H_{20} - nO_{10} - n(O.NO_2)n$$

Although difficult to prepare the individual esters without admixture of lower and higher nitrated derivatives, Eder gives the following as the properties of the nitrates which he was able to obtain.

Cellulose Hexanitrate. (C_{12} formula.) Cotton dried at 100° is, after cooling, introduced into a mixture of 3 volumes sulfuric acid, sp. gr. 1.845, and 1 volume nitric acid, sp. gr. 1.50, the mixture having been cooled to 10°. No more cotton is to be introduced than can readily be immersed, the latter being left to macerate in the acid for 24 hours with frequent stirring and kneading. It is then taken out, pressed, thrown into a large excess of water, washed by squeezing until it ceases to feel hot, then soaked for several days in frequently renewed water, and finally washed with hot water. 100 parts of cotton yielded 175–180 parts of guncotton, a small amount of which was soluble in ether-alcohol; soluble in nitrobenzene, insoluble in glacial acetic acid or in methyl alcohol free from acetone; and of industrial value only for ballistic purposes. Its ignition point varies between 160°–170°. Whereas ordinary guncotton may contain up to 15% ether-alcohol soluble cellulose nitrate, the hexanitrate appears to be the only one quite, if not entirely, insoluble in alcohol-ether.

Cellulose Pentanitrate. It is very difficult to prepare this nitric ester in the pure state by the direct action of nitric acid upon cellulose either alone or in the presence of a dehydrating agent. According to Eder, the pentanitrate may be prepared almost pure by dissolving pyroxylin in warm nitric acid and precipitating the clear solution by sulfuric acid after cooling the solution to zero or lower, this property having been discovered by De Vrij. Upon addition of sulfuric acid the solution becomes yellow, and afterwards turbid, when the solution is rapidly cooled.

After precipitation by four volumes of sulfuric acid of sp. gr. 1.84, the ester is separated and washed in the usual manner. It may be further purified by adding a large bulk of water, washing free from sulfuric acid, dissolving in ether-alcohol, and again precipitating with water. This process is continued until the nitrogen percentage remains stationary upon further treatment. This ester is readily soluble in ether-alcohol or acetone, less so in acetic acid, and insoluble in ethyl alcohol. Chloroform, carbon bisulfide or amyl acetate are said to have but little solvent effect upon it. Reduction to the dinitrate readily takes place by treatment with a concentrated solution of sodium or potassium hydroxides.

Cellulose Tetranitrate and Trinitrate, which are the most soluble forms of collodion cotton, are generally produced together on the manufacturing scale and are the nitrates of maximum industrial importance, are formed when cellulose is heated with a more dilute nitric acid, but at a temperature higher than that required to produce the hexanitrate. A product consisting mostly of the tetranitrate is obtained by treating cotton with a mixture of 1 vol. sulfuric acid, sp. gr. 1.845, and 1 vol. nitric acid of sp. gr. 1.380, at a temperature of 65° for 15 minutes. A trifle less nitrogen is contained in the product obtained by treating cotton with equal volumes of H_2SO_4 1.845, and nitric acid 1.400 for 15 minutes at 80°. Schering's celloidin has the composition of the tetranitrate.

On account of their equal solubility in ether-alcohol, acetone, amyl acetate, ethyl acetate, nitrobenzene, and other liquid and solid cellulose nitrate solvents, it is difficult, and probably impossible to separate one from the other. On treatment with concentrated nitric and sulfuric acids, additional nitrogen is taken on, and the penta- and hexanitrates result. Conversely, reduction to the dinitrate stage takes place by means of treatment with NaOH or KOH.

Cellulose Dinitrate may be formed by cautiously reducing the higher nitrates, or by the action of hot and dilute nitric acid upon cellulose. This ester readily dissolves in ether-alcohol or acetone, and is also said to dissolve in absolute ethyl alcohol. If so, and there are cellulose nitrates readily producible on a manufacturing scale which will do so, this is probably a distinguishing test for this nitrate alone. The continued action of alkalis on the dinitrate failed to produce the next lower body—cellulose mononitrate—treatment resulting in an entire decomposition of the ester into modified cellulose, organic acids and undetermined bodies.

While the classification of Eder made it much easier to satisfactorily explain the nitrocelluloses produced by him and his contemporaries, yet as it gave a maximum nitrogen content of 14.14% to guncotton—an amount never realized in practice—the subject was again investigated by Vieille in 1883.

Researches of Vieille. Eder raised the formula of the highest procurable cellulose nitrate to "hexanitrocellulose," although, of course, the percentage composition remained unchanged. Vieille,[1] however, working along similar lines, found the six possible compounds of Eder did not satisfactorily explain the percentages of nitrogen which he obtained, and in order to express them in chemical terms, was obliged to double the formulas. Therefore the highest obtainable nitrate was considered as a dodeca-derivative, and its formula expressed as $C_{24}H_{28}O_{20}(NO_2)_{12}$ from the parent cellulose molecule $C_{24}H_{40}O_{20}$ (see p. 14). His classification of the cellulose nitrates is expressed as follows.

Degrees of Nitration "Vieille"	Formula	Nitrogen %	Cc NO per Gm
1.—Dodecanitrocellulose .	$C_{24}H_{28}O_{20}(NO_2)_{12}$	14 14	225 6
Endecanitrocellulose	$C_{24}H_{29}O_{20}(NO_2)_{11}$	13 48	215 0
Decanitrocellulose .	$C_{24}H_{30}O_{20}(NO_2)_{10}$	12 76	203 5
Enneanitrocellulose	$C_{24}H_{31}O_{20}(NO_2)_9$	11 97	190 9
2.—Octonitrocellulose .	$C_{24}H_{32}O_{20}(NO_2)_8$	11 12	177 3
Heptanitrocellulose	$C_{24}H_{33}O_{20}(NO_2)_7$	10 18	162 4
Hexanitrocellulose	$C_{24}H_{34}O_{20}(NO_2)_6$	9 15	146 0
Pentanitrocellulose	$C_{24}H_{35}O_{20}(NO_2)$	8 02	127 9
3.—Tetranitrocellulose	$C_{24}H_{36}O_{20}(NO_2)_4$	6 77	107 9
4.—Cellulose . .	$C_{24}H_{40}O_{20}$	0	0

He found, however, that the highest nitrate which he was able to produce contained but 13.47% nitrogen, and therefore the older trinitrocellulose was not included in his list, but the following eleven only: Guncottons, endeca-, and decanitrocellulose; Collodions, Ennea-, octo-, and heptanitrocellulose;

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[1] Compt rend 1882, **95,** 132, Mem. des poudres et salpetres, 1884–1889, **2,** 217, abst Proc. U. S Nav. Inst 1882, **8,** 668; Chem. Ind 1882, **5,** 349, Chem Tech Rep 1882, **21,** II, 176, Chem News, 1882, **46,** 66; J. C S. 1882, **42,** 1184, Dingl Poly. 1882, **246,** 540; Chem. Centr. 1882, **53,** 632; Bull. Soc. Chim. 1883. **39,** 527; J. S C. I 1882, **1,** 516, Jahr. Chem 1882, **35,** 1187. See also Rev. Sci. 1882, **30,** 156 Arms Expl. 1898, **6,** 76; 1901, **9,** 175.

friable collodions, hexa-, penta-, and tetranitrocellulose; the derivatives below the above not being prepared by him.

Vieille's statements are tantamount to asserting that the highest obtainable cellulose nitrate, also of insoluble guncotton, cannot contain over 13.47% nitrogen, and this, together with the classification of decanitrocellulose as an insoluble nitrocellulose, have since been conclusively refuted and proven inaccurate beyond dispute.

From his experiments it appears that the most important factor in determining definite and controllable results in cellulose esterification is the concentration of the nitric acid, which was the principal variant quantitatively investigated. The temperature of nitration was kept constant at 10°–11°, and a large amount of nitric acid (from 125 to 150 times the weight of the cotton) was employed, in order that rise in temperature or dilution of acid from water given off in the reaction, would exert a minimum effect upon the components of the esterifying system. The products which were analyzed by a modified Schloesing method, are expressed in cc. NO_2 gas under standard conditions, calculated to 1 gm. of ester, and are indicated in Table CV.

The length of exposure of the cotton was determined in each instance, and was always under control. P. Vieille found with the acid $HNO_3.\frac{1}{2}H_2O$ (1.488 sp. gr.) that after forty-eight hours' immersion, the product was still blued with iodine, and gave 161 cc. NO_2, but after sixty-two hours' treatment (when the iodine reaction could not be obtained), the product contained 165.7 cc. NO_2. He concludes that the explosive properties of the cellulose nitrates are in direct relation to the completeness of nitration, that with decrease of nitric acid absorbed by the cellulose molecule decrease in combustion results, and increase of carbonaceous residue as the final result. For practical purposes, the classification into three groups is made, the "guncottons," "collodions," and "friable cottons."[1] The stability decreases with decrease of nitric acid content, with respect to reagents such as hydrochloric acid and ferrous salts. With products of low nitration, the decom-

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[1] According to Vieille the measurement of pressures developed by the products in closed receptacles showed that the force diminishes correspondingly with a decrease of nitrogen. Thus a collodion cotton yielding 184 cc NO produced pressures inferior by one-fifth those furnished by a guncotton of 211 cc. Therefore the percentage of nitrogen constitutes a true measure of the explosive qualities of the nitrate.

Table CV.—Cellulose Nitrates According to Vieille

Density of HNO_3. 15°	Composition of the Acid	No. of Cc. of NO_2 Evolved by 1 Gm of the Nitrated Product, 0°; 760 Mm.	Remarks
1.502 1.497	$HNO_3 + 1.5H_2O$ " "	202.1 197.9	The nitrated product resembles cotton. It is completely soluble in acetic ether; very slightly soluble in pure ether or ether-alcohol
1.496 1.492 1.490	$HNO_3 + 1.68H_2O$ " " $HNO_3 + 1.85H_2O$	194.4 187.3 183.7	Soluble completely in acetic ether and ether-alcohol. The fiber is not attacked. Collodion cotton
1.488 1.483	$HNO_3 + 2.7\ H_2O$ $HNO_3 + 2.13H_2O$	165.7 164.6	The nitrated product has the same appearance as cotton. It becomes gelatinous through the action of acetic ether and ether-alcohol. Solutions more gelatinous
1.476 1.472 1.469	$HNO_3 + 2.27H_2O$ " " $HNO_3 + 2.50H_2O$	141.1 140.0 139.7	Cotton dissolves in the acid produces a viscous liquid precipitable by water. The product thus obtained swells up, through the action of acetic ether, and becomes gelatinous without dissolving. Ether-alcohol produces no effect
1.463 1.460 1.455 1.450	$HNO_2 + 2.50H_2O$ $HNO_3 + 2.76H_2O$ " " $HNO_3 + 3.08H_2O$	128.6 122.7 115.9 108.9	The product is extremely friable, and is collected in the form of a paste. Neither acetic ether nor ether-alcohol produces any effect upon it. Strongly colored by I in KI solution
1.422 1.430	$HNO_3 + 3.08H_2O$ " "	108.9	Residue becomes more and more friable, and is strongly blackened by the action of iodine solution. Nitration, insignificant

position commences in the cold; with mean nitration a few minutes' heating is required, while with the products yielding more than 200 cc. nitrogen dioxide per gram, sustained ebullition is required to induce decomposition. These nitrates, then, appear to acquire a maximum of stability along with a maximum of power.

Vieille employed sulfuric acid of sp. gr. 1.832, and nitric acid of sp. gr. 1.316, and the absorbent cotton prepared for pharmaceutical uses. The nitric acid was treated at a temperature of 70° with dry CO_2 gas for several hours in order to expel the nitrous fumes, while 4 gm. samples of cotton were used in the experiments. The acid mixture was placed in a flask which could be closed, the cotton added, and the contents thoroughly shaken in order to insure intermingling as nearly instantaneous as possible. After shaking the flask was allowed to remain in water at 18°–19° for periods of 6, 12, and 24 hours, respectively, then washed to neutrality in the usual manner. Twenty-five separate experiments satisfactory to the author were made, the results of each being shown in Table CVI.

A critical examination of the results shown in this table indicates that the mixtures in which the proportion of nitric acid is low (as in mixtures 5 and 6) give, even after 12 hours' reaction, an incompletely nitrated product, which is not completed even after 24 hours. These mixtures, therefore, must be considered as not ideal.

In a second series of experiments the temperature of esterification was maintained at 7° 8°, the other factors being substantially the same except that they contained but 5% water, but it was noted that with the reduced temperature saturation proceeded much more slowly. The results are shown in Table CVII

The investigations of Vieille in their entirety, undoubtedly constitute one of the most important contributions on the chemistry of the cellulose nitrates which had been published up to that time.

Bruley[1] supplemented the researches of Vieille, first by a careful analysis from a practical viewpoint of the theoretical considerations deduced, and then carried the subject further by examining into the effect which the several variants of the esterizing bath exerted upon the finished product, as well as the influence of the treatments of washing, pulping, etc., i. e., the processes to which the ester was subjected after nitration. His results possess a practical utility aside from the theoretical considerations. He demonstrated that in the process of nitration, while still keeping

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[1] Mem. Poudre et Salpetres, 1895–1896, **8**, 111; abst Meyer Jahr. Chem. 1897, **7**, 301.

TABLE CVI —NITRATION EXPERIMENTS OF VIEILLE

	Mixture			6 Hours			12 Hours			24 Hours		
	H_2SO_4	HNO_3	H_2O	Nitrogen	Solubility	Viscosity	Nitrogen	Solubility	Viscosity	Nitrogen	Solubility	Viscosity
				Cc	per 100	S	Cc.	per 100	S	Cc.	per 100	S
1	100	55.2	30.7	194.8	97.3	105	194.2	97.3	129	"	"	"
2	"	45.9	24.7	202.2	16.0	"	205.0	7.7	"	"	"	"
3	"	37.1	18.8	"	"	"	209.6	2.0	"	211.0	1.2	"
4	"	18.2	13.6	"	"	"	204.8	2.2	"	208.8	1.7	"
5	"	9.2	12.9	"	"	"	121.4	20.8	"	141.0	18.5	"
6	"	8.8	22.8	"	"	"	123.4	59.5	"	129.9	54.7	"
7	"	18.0	22.5	188.8	90.4	"	193.2	92.0	"	"	"	"
*8	"	18.3	33.2	"	"	"	"	"	"	"	"	"
9	"	28.0	23.5	197.8	83.5	105	200.4	80.4	129	"	"	"
10	"	36.6	29.8	186.6	96.1	141	187.4	96.5	92	"	"	"
11	"	54.9	39.2	162.2	90.5	"	166.8	92.3	"	"	"	"
12	"	46.0	34.4	177.2	96.1	60	178.2	94.1	72	"	"	"
13	"	27.4	33.7	153.4	36.1	"	154.6	41.2	"	"	"	"
14	"	37.2	38.2	148.4	19.1	"	148.2	25.4	"	"	"	"
15	"	46.4	44.3	141.2	2.5	"	141.2	2.9	"	"	"	"
16	"	54.6	35.6	178.0	96.9	78	178.6	97.2	70	"	"	"
17	"	45.3	30.2	189.8	97.7	91	190.6	98.4	88	"	"	"
18	"	44.9	39.2	151.4	26.9	"	155.2	24.1	"	"	"	"
19	"	36.6	21.7	198.0	92.9	"	199.6	81.9	"	"	"	"
20	"	36.2	34.4	166.8	86.3	91	170.8	93.2	88	"	"	"
21	"	27.4	18.5	209.0	4.8	"	210.0	3.9	"	"	"	"
22	"	27.6	28.4	184.4	95.2	37	187.4	96.2	69	"	"	"
23	"	18.4	18.2	"	"	"	204.4	8.5	"	207.8	7.0	"
24	"	18.1	27.8	167.6	92.2	46	169.6	96.5	82	"	"	"
25	"	39.9	17.6	"	"	"	196.6	24.5	"	198.6	11.0	"

* In No 8, cotton dissolved in acid mixture

TABLE CVII NITRATION EXPERIMENTS OF VIEILLE

	Composition of Mixture			Results Obtained during a Reaction of								
				6 Hours.			12 Hours			24 Hours		
	H₂SO₄	HNO₃	H₂O	Nitrogen Cc	Solubility per 100	Viscosity S	Nitrogen Cc	Solubility per 100	Viscosity S	Nitrogen Cc	Solubility per 100	Viscosity S
1	100	59.1	29.6	204.0	55.3	"	203.8	46.5	"	"	"	"
2	"	49.1	24.3	"	"	"	211.0	2.0	"	211.0	2.1	"
3	"	39.6	18.8	"	"	"	211.6	1.1	"	211.6	1.5	"
4	"	19.4	14.2		"	"	209.2	3.4	"	209.2	4.2	"
5	"	9.7	14.3	"	"	"	173.4	17.8	"	183.8	16.1	"
6	"	9.4	24.2	"	"	"	171.8	82.1	18	179.2	94.8	22
7	"	19.1	23.4	199.2	73.7	"	199.2	66.6	"	"	"	"
*8	"	19.5	34.2	"	"	"	"		"	"	"	"
9	"	29.8	23.9	206.8	11.9	"	206.8	9.5	"	"	"	"
10	"	39.0	29.8	192.4	98.5	128	193.4	97.6	145	"	"	"
11	"	58.9	38.5	178.4	96.6	67	179.2	95.6	69	"	"	"
12	"	49.2	34.1	186.8	96.9	81	157.0	96.0	80	"	"	"
13	"	29.3	34.2	170.4	96.0	43	178.2	94.9	71	"	"	"
14	"	39.9	38.4	169.4	93.1	61	170.4	96.3	57	"	"	"
15	"	49.7	43.2	157.6	73.8	"	157.6	85.6	"	"	"	"
16	"	58.3	54.4	192.6	97.5	124	195.2	98.8	202	"	"	"
17	"	48.5	29.7	200.4	97.4	256	201.8	94.2	322	"	"	"
18	"	48.2	39.1	173.4	96.1	80	174.8	96.5	[illegible]	"	"	"
19	"	39.0	24.5	209.0	3.3	80	207.6	3.6	66	"	"	"
20	"	38.8	34.1	183.4	98.4	116	184.0	91.6	85	"	"	"
21	"	29.[illegible]	19.0	"	"	"	210.0	1.5	"	210.8	1.5	"
22	"	29.5	28.9	195.6	98.1	123	195.6	94.0	110	"	"	"
23	"	19.6	19.1	"		"	209.8	4.4	"	209.8	2.7	"
24	"	19.4	29.0	175.4	95.8	55	180.8	97.1	43	"	"	"
25	"	14.9	18.7	"	"	"	207.8	6.6	"	207.8	5.5	"

* In No 8 all cotton dissolved in acid

until no further loss in weight occurred and kept in a desiccator until used. The ash averaged 0.06%.[1]

The highest stage of nitration was obtained by using 2.5 gm. cellulose, 30 gm. nitric acid (sp. gr. 1.52) and 90 gm. sulfuric acid (sp. gr. 1.84) at a constant temperature of 15° during twenty-four hours, the nitrogen content varying from 13.37%-13.1%, which approaches closely (13.48%) to the endecanitrocellulose, and accords with the highest nitrogen product of Vieille (13.12%),[2] J. Eder (13.91%)[3] and L. Vignon (13.35%).[4] Variation of the temperature within the limits 0°-40° did not produce higher nitrogen percentages, from which the conclusion is reached that the endecanitrate is the maximum obtained by nitration with a mixture of nitric and sulfuric acids. Increasing the quantity of sulfuric acid lowered the nitrogen content, while decreasing it caused a slight rise in nitrogen. However, by using the method of C. Hoitsema[5] a nitrate containing 13.90% was obtained, sufficiently near to the percentage for dodecanitrate (14.14%).[6] However, in later experiments with Bebie, Lunge demonstrated that with acid mixtures containing as high as 11.34% water, a

[1] The acid mixtures in each instance were made from weighed quantities of "chemically pure" sulfuric acid, sp gr 1 84, and fuming nitric acid, sp. gr. 1 52, the former showing 95 62% H_2SO_4, the latter 93 76% HNO_3, and from 1%-2% lower oxides of nitrogen which were removed in the ordinary way.

[2] Compt. rend 1882, **95,** 132, Mem. des poudres et salpetres, 1881-1889, **2,** 217, abst Proc U S Nav Inst 1882, **8,** 668, Chem Ind 1882, **5,** 349; Chem. Tech Rep 1882, **21,** II, 176; Chem. News, 1882, **46,** 66; J. C. S. 1882, **42,** 1184, Dingl Poly. 1882, **246,** 540, Chem Centr. 1882, **53,** 632; Bull Soc. Chim 1883, **39,** 527, J. S C I 1882, **1,** 516; Jahr Chem 1882, **35,** 1187. See also Rev Sci 1882, **30,** 156. Arms Expl 1898, **6,** 76; 1901, **9,** 175. See also L. Vignon, Compt rend. 1903, **136,** 818

[3] Ber 1880, **13,** 169, 186, abst J. C. S. 1880, **38,** 372; Zts. Chem. Grossgew. 1879, **4,** 287, 1880, **5,** 42, Jahr. rein Chem 1880, **8,** 492; Bull. Soc. Chim 1881, **35,** 79, Sitzber. Akad Wissen. 1879, **79,** 537; Wag. Jahr. 1879, **25,** 390, J A C S 1880, **2,** 173; Jahr Chem. 1880, **33,** 1005; Indbl. 1880, 350; Chem. Ind. 1880, **3,** 246; Chem Tech. Rep. 1880, **19,** 338, Dingl. Poly. 1880, **237,** 254, Amer J. Sci 1880, **19,** 405.

[4] Compt rend 1898, **126,** 1658, **127,** 872, abst. Bull. Soc. Chim 1898, **19,** 857, J S C. I. 1898, **17,** 794; 1899, **18,** 81; Chem. Centr. 1898, **69,** II, 422, 1246; Jahr. Chem. 1898, **51,** 1378.

[5] Zts. ang Chem 1898, **11,** 173, abst. J. S. C. I. 1898, **17,** 374; Mon. Sci. 1898, **51,** 500; Chem Centr. 1898, **69,** I, 780; Jahr. Chem. 1898, **51,** 1377; Wag. Jahr 1898, **44,** 383.

[6] H. Warren (Chem News, 1896, **74,** 239; abst. Mon. Sci. 1898, **51,** 52, Rev Sci 1897, **8,** 255, Chem Centr 1897, **68,** I, 214; Chem Tech. Rep. 1896, **35,** II, 498, Chem Ztg. Rep. 1896, **20,** 298, Meyer Jahr. Chem. 1896, **6,** 309; 1897, **7,** 304, 305, Tech. Chem Jahr. 1897-1898, **20,** 152; Wag. Jahr. 1896, **42,** 412) formation of "tetranitrocellulose" from the trinitro- and phosphoric anhydride has never been corroborated.

product containing 13.8% nitrogen can be obtained, which, however, is not stable, but gradually loses nitrogen until 13.5% nitrogen is reached, but remained perfectly constant at this point. It appears, therefore, from this investigator's work, that the endecanitrate is the highest stable form. The important observation was made and experimentally corroborated, that by lowering the proportion of water to a minimum[1] the percentage of nitrogen in the product is not raised, and that it is therefore useless to increase the expense in nitration by employing mixtures too high in total acid.

The influence of water on the nitrating process was determined by keeping the nitric and sulfuric acids practically constant,[2] and varying only the water content[3] The results are appended in the following table

No	Nitrogen %	Soluble in Ether alcohol* %	Yield Cotton %	Acid Mixture in H_2SO_4	HNO_3	Per cent H_2O
1	13.65	1.50	177.5	45.31	49.07	5.62
2	13.21	5.40	176.2	42.61	46.01	11.38
3	12.76	22.00		41.03	44.45	14.52
4	12.58	60.00	167.0	40.66	43.85	15.49
5	12.31	99.14	159.0	40.14	43.25	16.61
6	12.05	99.84	153.0	39.45	42.73	17.82
7	11.59	100.02	156.5	38.95	42.15	18.90
8	10.93	99.82	144.2	38.43	41.31	20.26
9	9.76	74.22	146.0	37.20	40.30	22.50
10	9.31	1.15	138.9	36.72	39.78	23.50
11	8.40	0.61	131.2	35.87	38.83	25.30
12	6.50	1.73		34.41	37.17	28.42

* Two parts ether and one part alcohol is intended when "ether alcohol" is specified

As is shown by the third column and might be expected, the products obtained were not chemically pure, but mixtures of various stages of nitration. The above results show the fallacy of attempting to judge of the ether-alcohol solubility of a cellulose nitrate from the nitrogen content. As these results indicate that a difference of a few per cent. of water may produce greatly differing stages of nitration, the explanation becomes clear that various nitrocelluloses must be produced where there is a chemical production of free water, and to minimize this variation the percentage of water so formed may be diminished by a large volume of nitrating acid, the variations decreasing with an increase in volume of acids.[1] No. 5 in the above table is a formula for the production of a collodion completely soluble in ether-alcohol and suitable for the production of photographic films, although the high percentage of nitric acid makes it an expensive mixture. From this table it appears that the group of entirely soluble cellulose nitrates, with a range of 12.31%-10.93% N, is obtained from acid mixtures ranging from 16.6%-20.3% water, and that the typical collodion cotton (octonitrocellulose of 11.13% N) requires 19.3% water in the acid mixture.[2] Below 10% N, it is seen, the solubility rapidly diminishes, while if the acid mixture contains 25% water or more, much unchanged cotton is left. In the beginning there is but little nitration, but much oxycellulose formed.[3] The morphological structure of the nitrate is greatly altered by an increase of water in the acid mixtures, above 18% water the fibers showing disintegration, the destructive action being at the maximum with 25% water.

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[1] Which was affected by the addition of oleum

[2] Thus introducing but one variable (water), whereas Vieille introduced two (water and nitric acid) and his results must therefore have depended upon both conjointly

[3] The small amount of water in the highest concentrations was made possible by adding free sulfur trioxide in the form of fuming sulfuric acid The temperature, duration of reaction, and proportion of cellulose to reacting mixture were kept practically constant.

In determining the influence of temperature on the nitrating process, it was found that rise in temperature rapidly increases the speed of the process, while the percentage of nitrogen decreases when passing from 15°-40°, but remains practically constant when nitrating from 60°-80°. By nitrating at higher temperatures the cellulose structure is materially changed and passes into solution in the reacting mixture. Best results in the production of a nitrate of 99% solubility in ether-alcohol were obtained by nitrating four hours at 40° in sulfuric acid 38 95%, nitric acid 42.15%, water 18.9%. In varying the proportion of sulfuric acid to nitric acid, Lunge found that with increase of the former the speed of the process rapidly decreased up to equal parts of each acid, while the maximum of nitrogen in the product is produced, f the proportion of sulfuric to nitric acid be not less than 1:4 nor greater than 3:1. Furthermore, above a certain proportion of sulfuric to nitric acids (approximately 8:1) the final product always contains cellulose, while an excess of sulfuric acid affects also the structure of the cellulose nitrate. In general, however, the larger the quantity of sulfuric acid in the nitrating fluid in comparison to the nitric acid, the slower the entire process is completed. Lunge's work showed that for the preparation of cellulose nitrate of practically complete ether-alcohol solubility, the proportion of equal parts of nitric and sulfuric acids with 19%-20% water in the mixture should not be exceeded. In corroboration of E. Bronnert[1] and L. Vignon,[2] it was noted that more dilute acid mixtures evidently resulted in the formation of oxycellulose, if not some nitrooxycellulose.[3] Of the cellulose nitrates obtained in the usual manner, products soluble in ether-alcohol may be obtained from 10.18% N (hepta-) up to decanitrocellulose (12.76% N), but the collodion and pyroxylin of commerce used for lacquers and artificial leathers and silk, range between hepta- and ennea-nitrocellulose (11.97% N), and where complete solubility is desired, nitrogen percentages from 11–11.5, with formula No. 7 in the preceding table.[4] The proportion of lower oxides

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[1] For this reason preparation of the cellulose nitrates by a centrifugal is of advantage inasmuch as the proportion of cotton to acid is as 1:50-55.

[2] The author is aware of substantially this formula having been used commercially by means of centrifugal nitration and with excellent results as regards uniformity in ether-alcohol solubility.

[3] This may be shown by the entire or partial solubility in dilute alkalis; precipitation from solution by acids or alcohols; intense coloring with basic dyestuffs; reduction with Fehling's solution and reaction with phenylhydrazine.

[1] Bull de Mulh 1900, 177, abst. J S C I 1900, **19**, 819, 820; Jahr. Chem 1900, **53**, 843, Chem Centr. 1900, **71**, II, 740

[2] Compt rend 1900, **131**, 509; abst Chem. Centr 1900, **71**, II, 811, J S. C I 1900, **19**, 1039, Mon. Sci 1900, **55**, 782, Jahr Chem 1900, **53**, 819; 1901, **54**, 892, Bull. Soc Chim. 1901, **25**, 130

[3] For each test 0.5 gm of the product under examination was heated on the water bath with 150 cc. of 0.5% solution methylene blue for an hour, and after cooling 100 cc compared with an equal volume of the original solution in a Lummer-Brodhuhn colorimeter, to ascertain the loss of coloring matter The results obtained indicated that the products formed with concentrated acids contain no oxycellulose, while dilute acids did result in its formation. The same result was obtained with Schiff's aldehydic group reagent—a solution of fuchsine decolorized by sulfurous acid

[4] A number of interesting experiments were made to determine the limits of ether and alcohol which could be varied from the 3.1 formula and still dissolve the nitrate. A 11.54% N-containing ester dissolved readily in 6E:1A, only 95% in 12E·1A, in the last case 324 cc ether to 26 cc. alcohol being required to dissolve 1 gm, which 26 cc. alcohol alone would not have done. 27E:1A dissolved but 7.3% when 1 gm was treated with 350 cc. combined solvent. In the other direction 1E 3A acted as a complete solvent, 1E:6A dissolved 93%, 1E.5A dissolved 95%, all of which goes to show that the proportions of these two liquids may be combined within widely varying limits from the commonly accepted proportion.

of nitrogen in the nitrating mixture had little, if any, influence on the yield or nitrogen percentage of the resulting product, as is indicated by the following results, in which the question of stability does not enter:

No.	NO_2 %	Nitrogen in Guncotton %	Yield %
1	0.13	13.55	174.53
2	0.99	13.50	175.02
3	1.84	13.56	173.98
4	5.15	13.56	175.60

While the presence of oxides of nitrogen in the products of Lunge did not decrease the stability as determined by the methods of Abel and Guttmann, it must be remembered that free nitrogen peroxide in the liquid form has a very destructive action upon cellulose.[1] These investigations in their entirety form one of the most valuable contributions to the subject of the formation of the cellulose nitrates.

With the object of ascertaining whether highly nitrated cellulose (13.5% N) is a true cellulose nitrate, oxycellulose nitrate, hydrocellulose nitrate, or a mixture of these substances, E. Berl and R. Klaye[2] undertook nitration experiments with cellulose, hydrocellulose and oxycellulose under precisely similar conditions so far as possible. The substances used were cellulose, hydrocellulose, hydralcellulose, and oxycelluloses prepared with potassium permanganate bromine, nitric acid, potassium chlorate, bleaching powder, and a new oxycellulose prepared by them by means of calcium permanganate, all of which, besides being freed from fat, were analyzed, microscopically examined, and tested with reagents such as methylene blue and Fehling's solution.

These products were then nitrated and were then examined by physical and chemical methods, the results being set forth in tables and graphic diagrams, showing that the authors have made a comparative study of the hydrocelluloses and oxycelluloses previously known; have prepared a new oxycellulose by treating cellulose in the cold with calcium permanganate; have formed the nitric esters of these substances under identical conditions and subjected them to comparative study; have demonstrated that the nitrate containing 13.5% N, obtained at ordinary temperatures, is a true nitric ester of cellulose; have shown that under these conditions the hydro- and oxycellulose nitrates obtained contain less N than the cellulose nitrate does; that the solubilities of the hydro- and oxycellulose nitrates in ether-alcohol are the same as that of the cellulose nitrate; that the absorptive powers of the hydro- and oxycellulose nitrates for methylene blue are much greater than that of cellulose nitrate; that the unnitrated materials fix much more methylene blue than their nitrates do, that the viscosities of acetone solutions of cellulose nitrates augment, for the same temperature and equal duration of nitration, with the N content; that the viscosities of acetone solutions of pure cellulose nitrates are superior to those of the hydro- and oxycellulose nitrates of the same N contents; and that the treatment of cellulose with hydrolyzing or oxidizing agents causes a breaking up of the complex cellulose molecule.

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[1] 100 gm liquid nitrogen tetroxide acting on 8 gm pure cotton during three days in a refrigerator, converted it entirely into a viscid mass mostly soluble in boiling water The solution reduced Fehling's solution on boiling, and reacted with phenylhydrazine, and lead, silver and barium salts

[2] Zts Schiess Spreng. 1907, **2,** 381; Chem Centr 1908, **79,** I, 1381; J. C. S. 1908, **94,** i, 504; Jahr. Chem. 1905–1908, 976; Wag Jahr 1907, **53,** I, 430, C. A. 1908, **2,** 184. Zts Schiess. Spreng. 1907, **2,** 403, Wag. Jahr 1907, **53,** I, 431; Jahr Chem. 1905–1908, 975; Chem. Centr. 1908, **79,** I, 1381, J C S 1907, **92,** i, 390, C A 1908, **2,** 898 Mon. Sci. 1910, **73,** 103.

Their results are epitomized in the following table:

	Nitrogen by Nitrometer	Nitrogen by Dumas	Atomic Ratios from Analyses C	H	N	O	Solubility in Et-Al	Methylene Blue Test	Viscosity
Cellulose	13.50	13.32	24.0	34.0	11.0	11.8	1.8	0.6	10,000.0
Hydrocellulose	13.23	13.36	24.0	36.6	10.9	42.1	12.15	2.4	65.7
Hydralcellulose	13.07		24.0	36.3	10.6	41.2	22.5	2.4	8.1
$KMnO_4$ O/c	13.31		24.0	32.8	10.8	41.5	18.0	1.6	5.2
Br O/c	12.92	13.29					15.5	3.5	9.1
$Ca(MnO_4)_2$-O/c	13.25		24.0	35.5	10.8	41.4	20.5	3.3	11.1
HNO_3-O/c	12.87	13.28	24.0	34.0	10.4	40.0	34.0	5.0	7.9
$KClO_3$-O/c	13.01		24.0	33.9	10.2	40.5	18.0	3.0	7.2

E. Berl and M. Delpy[1] have investigated the material extracted from cellulose nitrates in the course of manufacture by the alcohol used in removing the water from the pulped material, being obtained from the accumulation in the still from which the used alcohol was rectified. This residue when dried is a brown powder contaminated with iron oxide, and sodium and calcium salts from the wash water. When purified by solution in ethyl alcohol and precipitating with water, it forms a brown powder with an ignition temperature of 162°. About two-thirds are soluble in ethyl alcohol, evaporation of the latter leaving a yellowish residue, from which anhydrous ether fails to dissolve it. The molecular weight was determined as 1088, ignition temperature as 174°, and nitrogen 9.88%-10.06%. The fraction insoluble in ethyl ether is a violet-colored powder containing 9.45% N, and detonating at 157°. Stabilized nitrocellulose from which this alcohol-soluble material was obtained, had an ignition temperature of 181.5°. The fact that the real stability of a nitrocellulose is not obtainable from a determination of the ignition temperature alone was demonstrated by them on mixtures of purified nitrocellulose with 10% 20% of these unstable products. These alcoholic-soluble products are considered as nitric esters of "disintegrated cellulose material," the removal of which constitutes an additional purification treatment for the cellulose nitrates. The viscosity of the unstable material in 2% acetone solution was very little greater than that of pure acetone.

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[1] Zts. Schiess Spreng. 1913, **8**, 129; abst Wag Jahr. 1913, **59**, I, 457; J. S. C. I. 1913, **32**, 452; C A 1913, **7**, 2307. J. C. S. 1913, **104**, i, 1305; Chem. Zentr. 1913, **84**, II, 493, Meyer Jahr. Chem 1913, **23**, 363; Zts. ang. Chem. 1913, **26**, II, 447.

E. Berl and A. Fodor have contributed to the chemistry of the cellulose nitrates by a study of the nitrogenous decomposition products of the alkaline saponification of nitrocellulose, in which the authors—considering cellulose as a condensation of monose complexes—adopt a formula, $(C_6H_{12}O_6)n(n - 1)H_2O$, as the true cellulose formula, differing from that commonly accepted $(C_6H_{10}O_5)n$ by a greater amount the smaller the value of *n*.

Full details are given in experiments in which cellulose nitrate (12.3% N) was partially saponified with NaOH or alcoholic KOH to such an extent that no nitrogen-free aliphatic acids resulted as decomposition products. The nitrogenous bodies obtained indicated a strong breaking down of the cellulose structure, molecular weight determinations being possible in alcoholic solutions. This is further indicated by low viscosity in 2% acetone solution, 1.10-1.33 as compared with 13.5 for collodion cotton, and 9500 for highly nitrated cellulose.[1]

This product is designated as *cellon acid nitrate*, and is considered as derived from a product of lactonized glucosidohexonic acid, its formula being $C_{24}H_{33}O_{16}(NO_3)_5$, with a molecular weight of 887.3. It forms definite compounds with phenylhydrazine and bromophenylhydrazine, acid saponification yielding glucose and hexonic acid. Other bodies of a nitrite character were also separated, evidently the products of more advanced decomposition. The technical value of this study is in connection with the usual purification process for cellulose nitrate in smokeless powder manufacture, where the removal of free acid is hastened by boiling with dilute sodium hydroxide.

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[1] Zts. Schiess. Spreng. 1910, **5**, 313; Wag. Jahr. 1910, **56**, II, 440; J. S. C. I. 1910, **29**, 1083. Zts Schiess. Spreng. 1910, **5**, 254, 269; Chem. Zentr. 1910, **81**, II, 874; Jahr. Chem. 1910, **63**, II, 424; J. C. S. 1911, **100**, i, 264. Zts. Schiess. Spreng. 1910, **5**, 296; Chem. Zentr. 1910, **81**, II, 1039;

Thus may be produced these unstable alcohol-soluble compounds with an ignition temperature of 163°, and the liability to spontaneous decomposition increased. Their complete removal by long boiling with water or by alcoholic extraction will yield the *limit state* of stability.[1]

They afterwards found that the nitrogen compounds above described are intermediate products in the formation of a large number of non-nitrogenous compounds. Treatment of cellulose nitrate with 30% KOH causes rapid saponification, producing large amounts of oxalic acid and hydroxypyroracemic acid,[2] the latter acid being optically active, notwithstanding the statements of J. Aberson,[3] does not lose this property by long heating on the steam bath. This compound is evidently present both as COH-CHOH-COOH and CH_2OH-CO-COOH, the former being optically active, and readily decomposes to oxalic acid on standing. Cellulose nitrate when shaken for 24 hours with 10% KOH and the filtrate acidified, then precipitated with barium hydroxide, evolved large amounts of ammonia, and in the precipitate was separated and identified the barium salts of oxalic, malic, glycolic,

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Jahr. Chem. 1910, **63,** II, 425; C. A. 1910, **4,** 3138, 3139; J. S C. I. 1910, **29,** 978. For the alkaline saponification of alkylnitrates see P. Klason and T. Carlson, Ber. 1906, **39,** 2752; abst. Jahr Chem 1905-1908, II, 289; Chem. Centr. 1906, **78,** II, 1481; Meyer Jahr. Chem. 1906, **16,** 324.

[1] W. Will, Zts. ang. Chem. 1901, **14,** 743, 744, 783; abst. J. S. C. I. 1901, **20,** 932; J. Soc. Dyers Col. 1902, **21,** 1470, 1554; Mon. Sci. 1903, **59,** 117; Chem. Centr. 1901, **72,** II, 606, 667; Jahr. Chem. 1901, **54,** 894; Meyer Jahr. Chem. 1904, **14,** 369; Tech. Chem. Jahr. 1901, **24,** 204; Wag. Jahr. 1901, **47,** I, 501.

[2] W. Will, Ber. 1891, **24,** 400, 3871; abst. Chem. Ztg 1892, **16,** 1277; Meyer Jahr. Chem. 1891, **1,** 333. See also Zts physik Chem. 1899, **31,** 17.

[3] Zts. physik. Chem. 1899, **31,** 17; abst. J. C. S. 1900, **78,** i, 200; Chem. Centr. 1900, **71,** I, 328; Jahr. Chem. 1899, **52,** 143.

rihydroxyglutaric, and malonic acids, while the filtrate contained hydroxypyroracemic acid.

In an inaugural dissertation of W. v. Bonge, published in 904 in Leipzig, the work of Lunge and his co-workers has been mplified, especial attention being directed to the effect of varyng amounts of nitric and sulfuric acids upon the cellulose, as well s the effect of the water present, and including an attempt to determine the effect of anhydrous nitric and sulfuric acids on the eacting system. A mixture of 99.7% HNO_3 and 100% H_2SO_4 was employed, using sufficient of either/both for nitration so as o eliminate/overcome the possible effects of the water formed. Calculating that by the nitration of 5 gm. cellulose, 1.67 gm. water is formed, there was used 200-400 gm. mixed acid per 5 gm. cotton.

As it had been noted that strong acid alone will completely dissolve cellulose with corresponding decomposition and hydrolysis; and as concentrated nitric acid will produce products of a xyloidin nature; this work attempts to prevent the above decomposition of the nitric by the addition of the right amount of sulfuric, and to add sufficient nitric to prevent hydrolysis by the sulfuric; and also to determine the amount of sulfuric acid necessary to add to the nitrating bath to prevent the formation of gelatinous products. Furthermore, it was endeavored to ascertain what molecular ratio of one acid to the other was necessary in order to produce a cellulose ester at all, and what that minimum percentage of nitrogen would be. In endeavoring to separate cellulose from nitrated cellulose by means of cuprammonium solution, he found that both were practically equally soluble in this reagent, and that for this purpose it was valueless. He thereupon separated the unchanged cellulose by dissolving the nitric ester by means of sodium alcoholate in acetate solution, which, in 20-30 minutes at 40°-50°, dissolved the ester, leaving the original cellulose behind.

The cotton used was rendered absorbent by treatment with 20% sodium carbonate, and had a constant ash of 0.06%. Vacuum nitration (to assist acid penetration) was used, the temperature of reaction being 16°-17°, the time 15-16 hours. The ester was dried in dehydrated air at 31°, all weighings and storage of material being in the dark. The results obtained are shown in Table CXIII, and are unusually consistent and illuminating.

TABLE CXIII

Expt	Proportion H₂SO₄	Proportion HNO₃	Ccm NO per Gm	% N	% N after Deducting Unchanged Cellulose	Solubility in Ether-Alcohol 3 1	Amount of Unchanged Cellulose	Yield in % from Cellulose
1	10	1	.....	...				The substance dissolves
2	9	1	....	.....		..	...	
3	8	1	.	...				
4	7	1	50.35 50.73	3.16 3.18	5.1		37.79 37.72	Substance sometimes goes into solution Further obtained 56.6, 20.0
5	5	1	118.24 114.62	7.42 7.19	10.24		27.19 27.86	116.0
6	4	1	176.26 172.66	11.06 10.81		1.91	6.95 7.02	112.1
7	3	1	210.23 209.22	13.20 13.13				165.2
8	1	1	210.88 214.73	13.24 13.48		1.70	0.00	185.8
9	1	2	212.22 210.67	13.32 13.22			0.00	172.1
10	1	3	190.03 187.83	11.93 11.79		1.69	0.60	169.2
11	1	4	207.61 205.02	13.03 12.87		1.10	0.00	167.5
12	1	8	203.05 205.95	12.74 12.93		1.94	traces	151.0
13	1	16	195.21 192.60	12.25 12.09				175.8
14	∞	∞	174.97 175.21	10.98 11.00		0.00	0.00	150.0

Chemistry of the Cellulose Nitrates. Investigations 1901–1910. L. Vignon[1] has experimented on the reduction of nitrocelluloses by ferrous chloride; two specimens, one prepared by the method of Lunge for obtaining the highest nitration and containing 13.89% N, the other prepared by the author's method,[2] and containing 13.4% N, were reduced by ferrous chloride and gave oxycellulose as the result. Direct experiment showed that this oxycellulose could not have been formed by the re-oxidation of reduced cellulose by nitrogen dioxide or ferric chloride formed during the reduction, for when cellulose was heated with ferrous chloride and nitric acid, no oxycellulose was produced. The difference in behavior between cellulose and such polyhydric alcohols as mannitol, is thus confirmed.

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[1] Compt rend 1900, **131**, 509, 530, 558, abst J C S 1900, **80**, i, 589, 628; Chem Centr 1900, **71**, II, 811, 891, Chem News, 1900, **82**, 169, J S C I 1900, **19**, 1039, 1045, Jahr Chem 1900, **53**, 849, Tech Chem Jahr 1900, **23**, 152 Compt rend, 1903, **136**, 818, 898, 969, abst. Chem. Centr. 1903, **74**, I, 1081, II, 238, Jahr Chem 1903, **56**, 1017, Meyer Jahr Chem 1903, **13**, 344 Bull Soc Chim 1904, **31**, 105, abst Jahr Chem. 1904, **57**, 1167, Chem. Centr 1904, **75**, I, 651, J S C I 1904, **23**, 202. L. Vignon and I Bay, Compt rend 1902, **135**, 507, abst Jahr Chem. 1902, **55**, 805; Bull. Soc Chim 1903, **29**, 507, Meyer Jahr. Chem. 1903, **13**, 345; Chem Centr 1902, **74**, II, 237, 1094 L. Vignon and F. Germ, Compt. rend 1901, **133**, 155, 540; abst. J. C. S 1901, **82**, i, 662, Jahr Chem 1901, **54**, 651, 652; J. S. C. I. 1901, **20**, 1244; Bull Soc. Chim 1902, **27**, 24, Chem Centr 1901, **72**, II, 1044; 1902, **73**, I, 456, Chem News, 1901, **84**, 202. L. Vignon and P. Sisley, Compt rend 1891, **113**, 701, abst Chem. Tech. Rep. 1891, **30**, II, 110, Deut Ind Ztg 1891, 423

[2] Compt. rend 1898, **126**, 1658, **127**, 872; abst. Bull. Soc Chim.

L. Vanino has shown[1] that if dry guncotton be impregnated with sodium peroxide and a few drops of water be then added, the guncotton is immediately ignited, but not detonated. Excess of water must be avoided, the reaction being considerably promoted by the addition of formaldehyde to the water. If to commercial formalin a small amount of sodium peroxide be added a violent detonation occurs, with destruction of the glass vessel. When the peroxide is added in too small amounts, only small sparks of flame appear unaccompanied by an explosion, or only a development of gas is observed; whereas with larger additions, the explosion occurs regularly, accompanied by a dull report.

In addition to his studies upon the xyloidins (see p. 1903), C. Haussermann has made a series of contributions to our knowledge of the cellulose nitrates in which he has found[2] that upon distillation with sodium hydroxide, the aqueous distillate contains, besides ammonia, an aldehydic substance which responds to the iodoform reaction. He has also demonstrated that when nitrocellulose is boiled with alkaline hydroxides, a compound boiling at 60° 80° first separates which appears to be an oxime of an aldehyde or ketone.[3]

He has shown that the first reaction between cellulose and

1898, **19,** 857, J. S. C. I. 1898, **17,** 794; 1899, **18,** 81; Chem. Centr. 1898, **69,** II, 422, 1246, Jahr. Chem 1898, **51,** 1378.

[1] Zts. ang Chem 1902, **15,** 1299; abst. J. S. C. I 1903, **22,** 49; Chem. Centr 1903, **74,** I, 265, Jahr. Chem. 1902, **55,** 1055; Tech. Chem. Jahr. 1903, **26,** 167 See also Ber. 1901, **34,** 1128; abst J S. C. I. 1901, **20,** 747; Chem. Tech Rep. 1901, **40,** 236; Chem. Ztg. Rep. 1901, **25,** 161; Jahr. Chem. 1901, **54,** 896; Tech Chem Jahr. 1901, **24,** 208.

[2] Ber 1903, **36,** 3956; 1904, **37,** 1624; abst. J. S. C. I. 1904, **23,** 36. Chem. Centr. 1904, **75,** I, 160, 1405; Jahr. Chem. 1903, **56,** 1017; 1904, **57,** 1168; Meyer Jahr Chem. 1904, **14,** 370; Wag. Jahr. 1903, **49,** I, 345; 1904, **50,** I, 357

[3] The portion coming over first was treated with potassium carbonate, and the oil which separated was distilled in vacuo at a temperature not rising above 40° C. In this way a colorless mobile liquid was obtained, which yielded iodoform with alkali and iodine dissolved in potassium iodide

nitric acid is an adsorption reaction, such as that described by E. Knecht[1] who obtained a compound unstable towards water, by a short immersion of cotton in nitric acid of sp. gr. 1.415 and drying over quicklime. But with longer periods of action with acid of this strength and even down to 1.36 sp. gr., esterification always takes place to a certain extent, the compounds produced being stable towards water. The tendency to esterification rises rapidly with increase in the concentration of the acid and becomes very pronounced with acids of 1.450 sp. gr. and upwards. At ordinary temperature, the quantity of acid being 100–200 times that of the cotton, the fibers swell strongly in acids of sp. gr. 1.450-1.463, and break down into little particles, with the production of small quantities of products soluble in the acid but for the most part precipitated on dilution. The cellulose nitrates so obtained, after 48 hours' action, contain no more than 6.5%-8% of nitrogen and are insoluble in ether-alcohol and acetone. Their microscopic appearance is partly fibrous and partly amorphous. Acids of 1.469-1.476 sp. gr. immediately dissolve loose cotton; the products are precipitated by water and contain 8%-9% of nitrogen; they are insoluble in the usual solvents. These products are amorphous and belong to the xyloidin group; denser forms of cotton tissues are not dissolved but only parchmentized. Acids of 1.48-1.50 sp. gr. convert cotton into the ordinary pyroxylins, containing 9%-12.5% of nitrogen without alteration of structure. More concentrated acids have a felting or parchmentizing action, and uniform products are not obtainable. At higher temperatures, on the water bath, nitric acid of 1.45 sp. gr. dissolves the cotton, and the modified nitrocellulose may be precipitated by dilution at the right moment; prolonged heating produces oxidation and decomposition. Dilute nitric acid of 1.3 sp. gr. on the water bath has an oxidizing effect

solution, but did not reduce ammoniacal silver nitrate solution. The residue consisted of a red resinous substance insoluble in water. The distillate appears to consist of the oxime-like compound of an aldehyde or ketone; it contains 5.4% of nitrogen, 56% of carbon, and 10% of hydrogen. A distillate capable of yielding iodoform is obtained from both fibrous and amorphous nitrocellulose, and also from other nitrated carbohydrates, e. g., nitro-inulin, nitrostarch, nitrolactose and nitroglucose (W. Will and F. Lenz, Ber. 1898, **31**, 68; abst. J. S. C. I. 1898, **17**, 271), and the nitro-amyloid obtained by G. Lunge and E. Weintraub by allowing nitric acid to drop into a solution of cellulose in sulfuric acid (Zts. ang. Chem. 1899, **12**, 448; abst. J. S. C. I. 1899, **18**, 705).

[1] Ber. 1904, **37**, 539; abst. J. S. C. I. 1904, **23**, 335.

on cotton, yielding a gelatinous oxycellulose and soluble products. Acid of 1.2 sp. gr. also disintegrates cotton and yields soluble oxidation products. At the ordinary temperature dilute nitric acid has an action similar in the main to that of the non-oxidizing mineral acids, and produces friable hydrocellulose. The vapors of nitric acid of 1.4 sp. gr. also produce hydrocellulose at the ordinary temperature, while those of highly concentrated acids have a pronounced esterifying effect.

In a similar manner to cotton as stated in the previous paragraph, C. Haeussermann found[1] that sulfite-cellulose is converted into nitro-compounds, with little alteration of structure, by the action of concentrated nitric acid. With acid of sp. gr. 1.495 the product contains 11.1% and with acid of sp. gr. 1.48, 9.6% N after 3-4 days' action. With a large excess of acid, the cellulose is converted almost completely into soluble products in the course of some months. The behavior with concentrated nitric acid of hydrocelluloses prepared from cotton-wool and sulfite-cellulose, respectively, by the action of cold nitric acid of sp. gr. 1.1 for about 1 year, was also studied. The hydrocellulose was dissolved only very slowly in the cold but very rapidly on warming with the concentrated acid. With acid of sp. gr. 1.5, 1.485, 1.48, and 1.4, in the cold, the cotton hydrocellulose yielded products containing 13%, 9.5%, 8.9% and 2.3% N, respectively, while the hydrocellulose from sulfite-cellulose, with acid of sp. gr. 1.495, 1.48, 1.45, and 1.4, yielded products containing 11.2%, 8.8%, 6.6%, and 2.1% N, respectively. Neither the highly nitrated sulfite-cellulose, nor the highly nitrated hydrocellulose, was completely soluble in acetone.

In respect to the fact previously mentioned of the existence of cellulose nitrates of the same nitrogen content which were, and were not dissolvable by ether alcohol, E. Divers[2] has advanced the opinion that in one case the material consisted of a product substantially the same chemically, whereas in the other, the result was produced by mixtures of nitrated celluloses of higher and lower nitrogen content, but of mean nitrogen percentage equal to the ester first stated. His reasoning sounds quite logical.

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[1] Zts ang. Chem 1910, **23,** 1761; 1913, **26,** 456, abst J S C. I. 1910, **29,** 1151, 1913, **32,** 885, C A 1911, **5,** 195, 1913, **7,** 3836, Bull Soc Chim. 1911, **10,** 85; Chem Centr 1910, **81,** II, 1289, 1913, **84,** II, 1295; Jahr. Chem. 1910, **63,** II, 423; Wag Jahr 1913, **59,** II, 543

[2] J. S C I. 1904, **23,** 297.

E. Knecht[1] has described a labile (unstable) cellulose nitrate obtained by the immersion of cotton yarn for 2 minutes in nitric acid of 1.415 sp. gr., washed and dried over CaO. The product formed is represented by the mass formula $C_6H_{10}O_5.HNO_3$, fuming in moist air, and being at once decomposed by water into HNO_3 and a cellulose which when air-dry contains 1% more water than the original. On heating this nitrate at 100° in vacuum, nitrous vapors are evolved and oxycellulose remains. If the treated yarn is washed with water after being removed from the acid, it has lost 13% of its length and acquired the property of mercerized cotton, from which the author deduces that it is probably cellulose hydrate.

E. Knecht and A. Lipschitz[2] find that the mercerization of cotton cellulose by concentrated HNO_3 (sp. gr. 1.415) takes place in two stages, an unstable nitrate of the approximate formula $C_6H_{10}O_5.HNO_3$ being formed almost instantaneously and later being transposed to stable nitrates, the N content of which increases to a certain maximum and then by continued contact with the acid decreases to a negligible quantity. The amount of N fixed by the cellulose depends on the concentration of acid, time of contact, and temperature of reaction. At 16° a maximum N content of 3.05% is reached after 32 hrs., after which the N content steadily decreases to 0.035% at the end of 8 months. Influence of temperature was studied between −10° and 60°. N content increases with temperature up to 31° where formation of oxycellulose commences, after which it decreases to 0.0% at 61° (3 hrs. immersion). The treatment of cotton with concentrated HNO_3 causes considerable shrinkage (about 13%) and increases the tensile strength. The latter effect diminishes as period of contact is increased, the cotton being of normal strength after 30 min. and having lost $^2/_3$ its normal strength after 32 hrs. Temperature of reaction also affects the strength of the product. The nitrated cotton does not differ from ordinary cotton in its behavior toward acetic acid, HCl and H_2SO_4; it is soluble

[1] Ber. 1904, **37**, 549, abst J. S C I 1904, **23**, 335, Meyer Jahr Chem. 1904, **14**, 368, Jahr Chem 1904, **57**, 1165, Chem Centr. 1904, **75**, I, 872

[2] J S C I 1914, **33**, 116, abst. C. A 1914, **8**, 1348; Chem. Zentr. 1914, **85**, I, 1557; J. C. S. 1914, **106**, i, 560; Zts ang. Chem. 1914, **27**, II, 567.

in 20% NaOH on warming, but on denitration with $(NH_4)_2S$ yields a cellulose insoluble in weak or concentrated NaOH. With 0.02 *N*/I, the nitrated product gives a brown-black coloration; with ammoniacal $AgNO_3$, yellow, and with Schiff's reagent, a deep red, indicating aldehydic properties. The Cu number is 31 to 33. Treatment with HNO_3 as described increases the affinity of cotton for all classes of dyestuffs, methylene blue forming a striking exception, and in general this affinity is stronger than that of cotton mercerized by NaOH.

B. Rassow and W. v. Bonge[1] have investigated the action of acid mixtures, containing varying proportions of 100% sulfuric acid and 99.7% nitric acid on cellulose, with a view to obtaining a pure nitrocellulose free from admixture with partial decomposition products and containing a high percentage of nitrogen. The results of the nitrations and the proportions of acids used are given in the following table:

	Acid Mixture Used for 5 Gm. of Cellulose			Solubility in Ether-Alcohol		Percentage Yield of Nitro-Product Referred to Original Cellulose
	H_2SO_4	HNO_3	Nitrogen %	3:1	Un-changed Cellulose	
1	300	30	....	.	...	Product
2	270	30	....	..	....	Dissolves
3	240	30	..	..	....	in the Acid
4	210	30	3.16		37.79	56.6
	.	.	3.18	...	37.72	20.0
5	250	50	7.42	...	27.19	116.0
			7.19	..	27.86	
6	280	70	11.06	1.91	6.95	142.4
			10.81		7.02	
7	300	100	13.20	....	.....	165.2
			13.13			
8	150	150	13.24	1.70	0.00	185.2
			13.48			
9	75	150	13.32	....	0.00	172.1
			13.22			
10	75	225	11.93	1.69	0.00	169.2
			11.79			
11	60	240	13.03	1.10	0.00	167.5
			12.87			
12	30	270	12.74	4.94	traces	151.0
			12.93			
13	15	240	12.25	....	.....	175.8
			12.09			
14	0	250	10.98	0.00	0.00	150.0
			11.00			

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[1] Zts. ang. Chem 1908, **21**, 732; abst. J. S. C. I. 1908, **27**, 523; J. C. S. 1908, **94**, I, 394; Chem Zentr. 1908, **79**, I, 2024; Meyer Jahr. Chem. 1908, **18**, 310; Wag. Jahr. 1908, **54**, I, 449.

The nitrocellulose was separated from unchanged cellulose by means of Lunge and Weintraub's method. The results attained show that, to obtain an ester perfectly insoluble in water, an acid mixture must be used containing for every 7 parts of sulfuric acid, at least 1 part of nitric acid. The nitrocellulose thus prepared, contains 37.79% of unchanged cellulose. With anhydrous acids, it was found impossible to obtain such highly nitrated products as with ordinary commercial acids. Nitrocellulose, when prepared with nitrogen pentoxide, is obtained as a gelatinous mass, and is difficult to wash. The solubility of the products obtained with anhydrous acids is generally small in the usual solvents for nitrocelluloses.

A. Saposchnikoff[1] considers the non-homogeneity of nitrocellulose to be largely due to the inevitable dilution of the nitration mixture during the progress of esterification from water liberated in the course of the reaction, the external parts of the mass or filaments being more highly nitrated than the inner parts.[2] He maintains that the final degree of nitration is materially influenced by the reversibility of the process. For instance, if the nitric acid employed is sufficiently concentrated to form nitric esters of cellulose, and if it is in tolerably large excess, then the chemical reaction proceeds very rapidly. Thus, with a mixture of 23.8% HNO_3, 71.5% H_2SO_4, and 4.7% water at 20°, it was found that after two minutes only 1.8% of the cellulose (cotton) remains unattacked, the nitrated portion containing 12.7% of nitrogen, corresponding to the introduction of ten NO_3, while after 5 minutes 11 NO_3 were introduced. These results, together with those obtained with a nitrating mixture composed of 30% HNO_3, 65% H_2SO_4, are in accord with those of G. Lunge and

[1] Seventh Int. Cong. Appl Chem 1909, IIB, abst. J. S. C. I. 1909, **28,** 747. J. Russ. Phys Chem. Soc. 1909, **41,** 1712; abst J. C. S. 1910, **98,** i, 156; J S. C I. 1909, **28,** 747; C A 1909, **3,** 2223 See Zts. Schiess. Spreng. 1909, **4,** 441; abst Meyer Jahr. Chem. 1909, **19,** 333. J. Russ. Phys Chem. Soc. 1906, **38,** 1192; abst. J. C. S. 1907, **92,** i, 390.

[2] The author (Worden) has comminuted purified cellulose (cotton) until microscopic examination showed over six million particles per gram, and nitrated this material at the same time, in similar apparatus, and as far as possible under identical conditions as to temperature and acid mixture, with samples of the same cellulose not comminuted, and was unable to determine by solubility determinations, viscosity or nitrogen percentage, that any difference exists as the result of finely dividing cellulose before nitration. If the above observations are correct, this would nullify the experience of Saposchnikoff on this point.

J. Bebie.[1] Ternary mixtures of sulfuric and nitric acids and water were investigated by determining the densities, electrical conductivities, and partial pressures of the vapors of nitric acid in the mixtures.[2] The results obtained indicate that in such mixtures there occurs a reversible process of the type:

$$HNO_3.nH_2O + H_2SO_4 \rightleftarrows HNO_3,(n - x)H_2O + H_2SO_4, x\,H_2O$$

which dehydration of nitric acid reaches a limit with a mixture of the composition corresponding with the equation:

$$HNO_3 + xH_2SO_4 + xH_2O = HNO_3 + x(H_2SO_4,H_2O)$$

and further addition of sulfuric acid was found to result in the formation of nitric anhydride. The results of these determinations are given in the form of a triangular diagram.

C. Piest has contributed a series of three articles on the chemistry of nitrocellulose as observed from the practical nitration of cotton, which may be considered as an extension of the work of Berl and Klaye (see p. 1662) and of Berl (see p. 1664), and in which the nature of the previous treatment of the cellulose was ascertained as influencing the properties of the nitrocellulose resulting therefrom. The first experiments perhaps have their value attenuated by the fact that they were laboratory results and made on small quantities, but the later work was with greater quantities. C. Piest[3] subjected cotton to the following treatments: (1) Bleaching for 48 hours in bleaching powder solution of 3.5° B.; (2) and (3) bleaching for 8 days in solutions prepared by mixing 2.5 and 5 kilos, respectively, of bleaching powder with 5 liters of water; (4) mercerization by treatment with 18.5% caustic soda lye for 20 minutes, (5) heating for 10 hours at 150° C. in a current of carbon dioxide.[1] The results obtained showed that with a given nitrating acid and temperature of nitration, the nitrocellulose prepared from strongly bleached cotton has a somewhat lower nitrogen-content and a considerably higher solubility in ether-alcohol than that prepared from ordinary cotton. The solubility of the nitro-compound in absolute alcohol increases as the cotton is more strongly bleached. Nitrocellulose from strongly bleached cotton is more difficult to stabilize than that from ordinary cotton. The stabilized nitrocellulose is more soluble in ether alcohol than the non-stabilized product. Nitrocellulose from mercerized cotton has a slightly lower nitrogen-content, a much higher solubility in ether-alcohol, about the same solubility in absolute alcohol, and is more difficult to stabilize than that from ordinary cotton. Nitrocellulose prepared from cotton which has been heated in a current of carbon dioxide has a slightly higher nitrogen content, about the same solubility in absolute alcohol and in ether alcohol, and is more difficult to stabilize than that from ordinary cotton.

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[1] J A C S 1901, **23,** 528, abst Zts ang Chem 1901, **14,** 483, Chem News, 1901, **84,** 30, J S C I 1901, **20,** 1021, Chem Centr 1901, **72,** II, 34, 92, 764, Jahr Chem 1901, **54,** 893, Meyer Jahr Chem 1901, **11,** 316, Wag Jahr 1901, **47,** I, 495 See also Zts Schiess Spreng 1906, **1,** 2, abst Chem Centr 1906, **77,** I, 714, 1907, **78,** I, 947, Jahr Chem 1905 1908, II, 974, Wag Jahr 1906, **52,** I, 487, C A 1907, **1,** 1622 Zts ang Chem 1907, **20,** 262, 1908, **19,** 2051 O Guttman, Chem Centr 1907, **78,** I, 1029

[2] A Saposchnikoff, J Russ Phys Chem. Soc 1903, **35,** 305, 1098, 1904, **36,** 518, abst Chem Centr 1904, **75,** I, 1322, II, 396, J S C I 1904, **23,** 865, J C S. 1904, **86,** ii, 251, 558; Bull Soc. Chim 1904, **32,** 362, 1905, **34,** 173, 787, Rep Chim. 1904, **4,** 383; 1905, **5,** 49, 145, Jahr Chem 1904, **57,** 461; Meyer Jahr Chem. 1904, **14,** 191, Zts physik Chem 1904, **49,** 697, Chem. Ztg 1904, **28,** 405, J. Russ Phys. Chem Soc. 1904, **36,** 669; abst. Chem Centr. 1904, **75,** II, 685, J S C. I. 1904, **23,** 935 See J Russ. Phys Chem Soc 1900, **32,** 375, 1903, **35,** 506; Chem Centr 1900, **71,** II, 708, 1901, II, 1330; J. C. S. 1904, **86,** ii, 614; Bull Soc. Chim. 1905, **34,** 1068; Rep Chim 1905, **5,** 186, Chem Ztg 1904, **28,** 574.

[3] Zts. ang Chem. 1909, **22,** 1215; abst. C. A. 1909, **3,** 2227; J. S. C I. 1909, **28,** 746, Bull Soc Chim 1909, **6,** 1165, Chem. Zentr 1909, **80,** II, 1090, Jahr Chem. 1909, **62,** II, 388; Mayer Jahr. Chem. 1909, **19,** 335, Wag. Jahr. 1909, **55,** I, 431.

In a subsequent investigation the action of NaOH, barium hydroxide, and ammonium sulfide upon the cellulose nitrates was inquired into.[2] The method of experiment, in the case of a solution of sodium hydroxide, consisted in allowing 1 gm. of the cellulose nitrate to remain in contact, at ordinary temperatures, with 50 cc. of $N/2$ solution of sodium hydroxide for periods varying from one to ten days. The amount of sodium hydroxide remaining at the expiration of the selected period of time was determined by titration with $N/2$ hydrochloric acid.

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[1] E Berl, D R P 199885, 1907, abst. J S. C. I 1908, **27,** 937; Chem. Zentr. 1908, **79,** II, 466, Chem Ztg Rep 1908, **54,** II, 355, Zts. ang. Chem. 1908, **21,** 2233

[2] Zts. ang Chem. 1910, **23,** 1009; abst C A 1910, **4,** 2570, J. C. S. 1910, **98,** i, 464; J S C I. 1910, **29,** 841; Bull Soc. Chim 1910, **8,** 1563; Chem. Zentr. 1910, **81,** 508, Jahr. Chem 1910, **63,** II, 423; Meyer Jahr. Chem. 1910, **20,** 327; Wag Jahr. 1910, **56,** I, 493; Zts. Chem. Ind Koll. 1911, **8,** 60. See also Zts ang. Chem 1908, **21,** 2497, abst. C. A. 1909, **3,** 485; Bull. Soc. Chim 1909, **6,** 232, Chem. Zentr 1909, **80,** I, 474; Jahr. Chem. 1905–1908, II, 973; Meyer Jahr Chem 1908, **18,** 309, Wag. Jahr. 1908, **54,** II, 368

The nitrogen content of the residue remaining after this treatment was also determined. The original nitrogen content of the cellulose nitrate made from normally treated cotton was 13.16% and the solubility in ether-alcohol under 10%. The cellulose nitrate prepared from highly bleached cotton had a nitrogen content of 12.71% and a solubility in ether-alcohol of 40.93%, while that prepared from mercerized cotton contained 12.96% of nitrogen and had a solubility of 21.84%. Some of the results obtained are given in the following table:

	N/2 Aqueous Sodium Hydroxide					
	Normally Treated Cotton		Highly Bleached Cotton		Mercerized Cotton	
Time of Reaction Days	Residue %	Nitrogen in Residue %	Residue %	Nitrogen in Residue %	Residue %	Nitrogen in Residue %
1						
2	64.64	13.17	8.99	11.44	66.6	12.58
3						
4	34.71	13.10	1.78	9.76	43.5	12.11
5	25.25	12.96				
6	....	....	0.62	0	28.42	12.13
7						
8	14.06	12.68	1.12	0	19.96	11.96
9						
10	8.78	12.25	0.80	0	13.30	11.26

	Solution of Ammonium Sulfide					
	Normally Treated Cotton		Highly Bleached Cotton.		Mercerized Cotton	
Time of Reaction Days	Residue %	Nitrogen in Residue %	Residue %	Nitrogen in Residue %	Residue %	Nitrogen in Residue %
1	60.82	2.70	50.09	2.57	60.14	2.16
2	55.08	0.56	40.80	0.33	53.27	0.57
3						
4	51.97	0	39.35	0	52.35	trace
5	.....	....	...	....		
6					52.83	0
7	49.75	0	39.58	0	trace	....
8	49.44	0	37.67	0	52.15	0
9	.....	....	....	....	.....	....
10	....	....	....	...	.....	....

Under the above conditions *N*/2 alcoholic solution of sodium hydroxide completely decomposed cellulose nitrate in four days, leaving only about 0.5% of residue. After eight days in contact with a saturated aqueous solution of barium hydroxide, some 56% of residue remained which contained 10.6% of nitrogen. When the different cottons used for preparing the cellulose nitrates were treated in the same manner, it was found that, at the end of ten days' immersion in *N*/2 sodium hydroxide solution, the amounts of residues were as follows: Normally treated cotton (96.97%), strongly bleached cotton (80.96%), and mercerized cotton (98.4%). The results obtained with a solution of ammonium sulfide were also very similar to the above. By the action of aqueous $N/2$ sodium hydroxide on collodion cotton containing 12.36% of nitrogen, it was found, at the expiration of four days' contact, that 30.44% of residue remained, while after eleven days only 9.65% remained unattacked, and this residue contained 11.15% of nitrogen. Collodion cotton was found to be completely denitrated by the ammonium sulfide solution within 48 hours, with the production of oxycellulose.

O. Guttmann[1] in general, has confirmed the observations of C. Piest as outlined above.

Developments in Chemistry of Cellulose Nitrates, 1911–1920. On the reputed existence of hydrate of nitrocellulose, T. Chandelon[2] has drawn the conclusion that the increased solubility of moist nitrate is not due to the presence of a hydrate, but merely to the fact that the water present dilutes the mixture of ether and alcohol, for practically the same results are obtained whether a moist nitrocellulose is used, or whether water is previously added to the solvent portion. Hence in order to obtain collodions with a constant viscosity at a definite temperature, it is essential that the quantities of dry nitrocellulose, solvent and water should remain constant.

A description of experiments made to determine the effect of variations in the proportions and concentrations of sulfuric and nitric acids in the mixed acid upon the stability of the nitration products from both cotton and prepared wood fiber has been made by H. Tedesco,[3] in which H_2SO_4 of 92% and 103%, and HNO_3 of 86.7% and 97% were used in the proportions of 1:1, 1:2, and 1:3. With 1 part cellulose to 40 parts mixed acid, and 3 hours' nitration at not to exceed 23°, followed by cold washing and 5 hours' boiling, the following results were obtained:

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[1] Zts. ang. Chem. 1909, **22,** 1717, abst. C A 1910, **4,** 109, abst. J. S. C. I. 1909, **28,** 1007; Bull. Soc. Chim 1909, **8,** 222, Chem Zentr. 1909, **80,** II, 1285; Jahr. Chem. 1909, **62,** II, 388; Meyer Jahr. Chem. 1909, **19,** 335; Wag. Jahr. 1909, **55,** II, 431.

[2] Bull. Soc. Chim. Belg. 1912, **26,** 495, abst C. A 1913, **7,** 1418; J. C. S. 1913, **104,** i, 18; J. S. C. I. 1912, **31,** 1202; Chem. Zentr. 1913, **84,** I, 392; Kunst. 1913, **3,** 69; Zts. ang. Chem. 1913, **26,** I, 268, 366 Bull Soc. Chim. Belg. 1914, **28,** 13, 24; abst. C. A. 1914, **8,** 1506; J S C I. 1914, **33,** 222; Chem. Zentr. 1914, **85,** I, 1315; Kunst 1914, **4,** 4, 25; Meyer Jahr Chem. 1914, **24,** 424; Wag. Jahr. 1914, **60,** I, 358; Zts. ang Chem. 1914, **27,** II, 503.

[3] Zts. Schiess. Spreng 1912, **7,** 474; abst. C. A. 1913, **7,** 891; J. C. S. 1913, **104,** i, 447; J. S. C. I. 1912, **31,** 1202; Chem. Zentr. 1913, **84,** I, 894; Chem. Ztg. Rep. 1913, **37,** 386.

1. With cotton a maximum of 12.53% N was obtained with 1 part 92% H_2SO_4 and 1 part 97% HNO_3. Wood cellulose under similar treatment gave a maximum of 12.78% N. With both materials, the use of fuming sulfuric acid or of weaker nitric acid, as well as of different proportions than those above mentioned, gave a lower nitrogen content.

2. The stability of the fourteen different products obtained from as many different acid mixtures, both from cotton and wood cellulose, was determined by the Will test (see p. 2350). The minimum decomposition was noted when $HNO_3 \cdot H_2SO_4 = 1:1$.

3. Vacuum nitration gave higher nitrogen percentages in the case of cotton (12.7%) but poor stability both with cotton and wood cellulose.

4. All the products prepared from wood cellulose gave poor stability tests.

5. The ignition temperature of the nitrocelluloses from cotton were 180°-190°; those from wood, 138°-153°.

6. On simply storing for 14 days at room temperature, nitrocellulose which had been washed but not boiled was reduced in nitrogen percentage from 12.21 to 11.55, while similar material boiled 5 hours fell under the same conditions from 12.53% to 12.45% N.

7. Experiments made to ascertain the action of different strengths of sulfuric acid on nitrocellulose showed that by 1 hour's boiling, 40% H_2SO_4 gave complete solution, 20% caused a loss of only 0.23% N, and 10% a loss of 0.17% N. All nitrogen determinations were made by the Schloesing method.

From various experiments with nitrocellulose, in the study of the decomposition by acids and alkalis, G. Meissner[1] deduced the following

The highest degree of nitration is attained by nitrating cotton at 20° C. with a mixture of equal weights of nitric acid (sp. gr. 1.5) and sulfuric acid (sp. gr 1.84). The percentage of nitrogen is increased by nitration in vacuo. Prolonging the nitration beyond two hours lessens the yield. The temperature of ignition in nitrocellulose, determined by heating slowly in an oil bath a tube containing the sample, varies from 180° to 190° C. and is 20°–25° higher than that found by dropping samples into the same tube while cooling, until explosion no longer takes place. Nitrocellulose consists of a mixture of cellulose nitrates, of which those with less nitrogen dissolve more readily in ether-alcohol, any insoluble residue containing more than 12% N. Fractional precipitation of an acetone solution of nitrocellulose by water gives precipitates differing only slightly in nitrogen content. Nitrocellulose can be boiled for a short time with acids of limited concentration without losing weight; the limits depend on the nature of the acid and its concentration, being greater for nitric than for sulfuric acid, and less for collodion cotton than for guncotton. If these limits are exceeded, loss of weight and of nitrogen occurs. It is stated that guncotton, when boiled with nitric acid of any concentration up to 30%, leaves a residue containing not less than 11.41% N, even when the loss in weight has been 50%. Complete decomposition of nitrocellulose with 96% sulfuric acid produces nitrogen acids and oxides, sulfur dioxide, carbon dioxide, oxalic, tartaric, and fatty acids (but not formic or acetic acids). Decomposition of nitrocellulose by alkalis produces sodium nitrate and nitrite, and organic sodium salts. With baryta, some carbonate is formed. Alcoholic caustic soda (20%) produces a pasty mass soluble in water. The quantity of nitrate formed could not be estimated by the nitron method (this vol., p. 979). High results were obtained, and the author suggests that nitron combines with a molecular compound of alcohol and caustic soda, $C_2H_5OH.NaOH$. Nitroglycerol is saponified more rapidly than nitrocellulose. Sulfur dioxide passed through a suspension of nitrocellulose in hot, air-free water is partially oxidized to sulfuric acid. Nitrocellulose dissolves in phenylhydrazine with evolution of gas and formation of a gelatinous reddish brown substance.

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[1] Zts Schiess Spreng 1913, **8,** 252, 269; abst C A. 1913, **7,** 3540; J. C. S. 1913, **104,** i, 1305, J S C I 1915, **34,** 576; Mon Sci 1915, **82,** 79, Chem Zentr 1913, **84,** II, 1208; Meyer Jahr Chem 1913, **23,** 362, Wag Jahr. 1913, **59,** I. 456.

A. Angeli[1] has found that nitrocellulose in the form of collodion cotton or guncotton is easily gelatinized by pyridine, a large proportion of the latter yielding dense liquids which have the appearance of collodion, and gradually diminish in viscosity until, after a few days at the ordinary temperature, they resemble in this respect the pure pyridine; this phenomenon serving to detect unaltered cellulose in the presence of the nitric ester. Treatment of the collodion cotton with only sufficient pyridine to moisten, yields a semi-solid, transparent mass with the appearance of caoutchouc, this also becoming continually more fluid until it is able to pass through the filter paper.

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[1] Atti accad. Lincei, 1919, **29**, I, 20, abst J C S 1919, **116**, i, 196, C. A. 1919, **13**, 3316, J. S C I 1919, **38**, 365-A Gazz chim ital 1919, **49**, I, 159, abst Chem Zentr 1919, **90**, III, 754

The yellow liquid thus formed smells strongly of pyridine, and with water gives an almost white mass, of resinous appearance, and which retains pyridine tenaciously. When freed from the latter by means of alcohol and dilute sulfuric acid, re-precipitated, washed, and dried over H_2SO_4, a white, amorphous powder results, easily soluble in acetone and to a less extent in ethyl alcohol; almost insoluble in ether and benzene. Yield about 80% of the collodion used. The compound contains 9%-10% N, resembling the product obtained by E. Berl and A. Fodor.[1]

In a study of nitrocellulose reported upon by R. Namias,[2] and the influence of prolonged bleaching upon its transformation into dinitrocellulose, 5 gm. of cotton of the best quality were treated in 200 gm. of a bath containing 60% of sulfuric acid, 24% of nitric acid, and 16% of water, for periods of 2, 4, 12 and 24 hours at 18° C. The nitrogen content of the four products was practically identical, viz., 11.80% to 11.92%, and all were completely soluble in ether-alcohol. The fiber is appreciably weakened if nitration is continued much beyond two hours, or if higher temperatures are employed, and the nitrocellulose is less suitable for making collodion, or for coating incandescent mantles, etc. All the samples burned instantaneously without leaving a residue. Cotton which had received excessive chlorine treatment showed no difference under the microscope and gave no evidence of tendering, but when nitrated under the same conditions, the percentage of nitrogen in the products varied from 9.80% to 10.37%, and the solubility in ether-alcohol was incomplete. A residue was left on burning, indicating the presence of unnitrated cotton. The author suggests that this may be due to the presence of oxycellulose in the over-bleached cotton.

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[1] Zts. Schiess. Spreng. 1910, **5**, 313; Wag. Jahr. 1910, **56**, II, 440; J. S. C. I. 1910, **29**, 1083. Zts. Schiess. Spreng. 1910, **5**, 254, 269; Chem. Zentr. 1910, **81**, II, 874; Jahr. Chem. 1910, **63**, II, 424; J. C. S. 1911, **100**, i, 264. Zts. Schiess. Spreng. 1910, **5**, 296; Chem. Zentr. 1910, **81**, II, 1039; Jahr. Chem. 1910, **63**, II, 425; C. A. 1910, **4**, 3138, 3139; J. S. C. I. 1910, **29**, 978.

[2] Mon. Sci. 1918, **85**, 5; abst. C. A. 1918, **12**, 996; J. S. C. I. 1918, **37**, 167-A; Chem. Zentr. 1918, **89**, I, 974.

According to A. Herve,[1] the stability of nitrocellulose is considerably affected by the value of the ratio H_2SO_4/HNO_3. By varying this ratio from 1:1 up to 5:1 the amount of fixed H_2SO_4 in the nitrocellulose increases from 0.0505% to 1.860%. The stability (Abel test) of the nitrocellulose after boiling 8 hours with H_2O varied inversely with the amount of H_2SO_4 in the nitrating mixture. Nitrocellulose can be stabilized by boiling with H_2SO_4 and HCl (0.2% to 1.0%), followed by boiling with a dilute alkali. The saponification of the impurities is, however, slow. More satisfactory results are obtained by boiling the nitrocellulose with 0.1% to 1% of its weight of $MgCl_2$ for 12 hours. Nitrocellulose so stabilized with $MgCl_2$ gave a test of over 60 min. (Abel).

Comparative nitrations of cotton showed definitely that as the percentage of water in the nitrating mixture is increased, the percentage of nitrogen in the pyroxylin diminishes, while a variation in the percentage of nitric acid in the nitrating mixture, within fairly wide limits, had very little influence on the percentage of nitrogen in the product, and the effect was not regular.[2]

On comparing the composition of the baths before and after nitration, it was found that the quantity of nitric acid removed was always slightly greater than the equivalent of the percentage fixed in the nitrocellulose. It is concluded that, although in the manufacture of soluble pyroxylin the effect of small variations in the percentage of nitrogen is not of vital importance, in the manufacture of guncotton such variations have a very considerable influence on the ballistic power, and the control of the percentage of water in the nitrating mixture requires the most urgent attention. The regeneration of old nitrating baths by the addition of sulfuric and nitric acids is performed on the basis of analyses of samples taken from large reservoirs which in the acids are mixed by the agitation of compressed air. Analyses have shown, however, that homogeneity in composition is not always easily obtained by this method of mixing, even when agitation is prolonged for several hours, and substantial variations have been found in the percentage of nitrogen, in the nitrated cotton produced with acid taken from different parts of the tank. The author has made a careful examination of Crum's method for the determination of nitrogen in nitrocelluloses, using the Lunge nitrometer. To obtain consistent results it is absolutely necessary to verify that the reaction with the mercury has been complete, by shaking again after the volume has been accurately read off. Generally, two vigorous shakings are sufficient, and there is no alteration in volume after a third, but if a change is noted the operation must be repeated until the result is constant. One of the principal causes of divergent results is inattention to the solubility of nitric oxide in sulfuric acid. This gas is only insoluble in sulfuric acid of 85% concentration; its solubility in stronger acid becomes very sensitive and reaches 0.035 cc. per cc. of acid in the case of 94% sulfuric acid. It is possible to arrange matters so that the acid in the tube after dissolving the nitrocellulose in 96% acid, has a final concentration of 85%.

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[1] Mon. Sci. 1918, **85**, 193; abst. C. A. 1919, **13**, 186; J. S. C. I. 1918, **37**, 718-A; Ann. Rep. Soc. Chem. Ind. 1919, **4**, 542; Chem. Zentr. 1919, **90**, II, 297.

[2] Mon. Sci. 1918, **85**, 241; abst. C. A. 1919, **13**, 516; J. S. C. I. 1919, **38**, 56-A; Ann. Rep. Soc. Chem. Ind. 1919, **4**, 540, 543; Chem. Zentr. 1919, **90**, II, 622.

Theory of Nitration. The entire theory and practice of the esterification of the carbohydrates rests at the present time upon an empirical basis and upon a series of assumptions and predications, and notwithstanding the multiplicity of investigations by chemists and physicists of keen discernment and indefatigable perseverance, no satisfactory general theory connecting the composition of the mixed acids, temperature fluctuations and degree of nitration with chemical constitution of the esters formed, has as yet been enunciated.

Some of the difficulties in the way of elucidating such a generalization are as follows:

1. The absolute molecular weights of cellulose and the inorganic and organic esters derived therefrom are at present unknown, and so far as the discernment of the author is a criterion, the indications are non-existent that the solution of this problem lies in the immediate future.

2. No form or type of cellulose, or of a cellulose ester or ether as a chemical individual has as yet been synthesized and the results reported upon, due to the fact that in the normal

nitration or acetylation process the increment of acid (in ester formation) and of alkyl (in ether formation) in the cellulose aggregate is progressive and by indefinite and indistinguishable stages, so that a series of esters and ethers results, in all probability admixed with relatively small amounts of degraded celluloses, as indicated by viscosity determinations.

3. Until the inner mechanics of cellulose orientation have been analytically determined, the spacial arrangements and configuration of the groups constituting the corresponding esters must remain in doubt.

4. Therefore so far as the normal process of esterification is concerned, the preponderance of dependable testimony at the present time is to the effect that a series of nitrates always results, being inseparably admixed with products resulting from a depolymerization of the cellulose complex incident to treatment with the constituents of the esterizing bath.

5. The laws of mass action, as comprehended by our present conception, cannot be applied to the system of acid mixture and cellulose nitrate, on account of the entire absence of homogeneity.

6. No cellulose nitrate or other un-degraded or unchanged cellulose compound has as yet been prepared pure in a crystalline state, nor has such a product been prepared which may be purified by distillation, sublimation or otherwise completely isolated.

7. It as yet has been impossible to place cellulose in solution in any manner, and recover from the solution by fractional precipitation or otherwise, a cellulose which has not been affected by the treatment.

8. No one has as yet propounded a law or generalization of the relationship between solubility, viscosity, stability and nitrogen content, which did not reveal glaring inconsistencies, and the researches on this phase of the subject have been most numerous, and have involved the expenditure of a tremendous amount of mental energy and patience.

9. And finally, the complexity of the reacting mass and the fact that its composition is constantly changing due to the increment of water from the normal esterification process; the use of a cellulose which in its natural state admittedly contains impurities, or if an attempt has been made to remove them the cellulose has surely been changed irrespective of how careful the

purification treatment may have been conducted; and bearing in mind that in addition to cellulose, acids, water, nitrated cellulose, nitrated, reduced and oxidized products other than cellulose, and perhaps the esters of these bodies, together with sulfonic and nitrosulfonic acid esters, only complicates the subject.

Inasmuch as the usual expedients of purification and elimination preceding a general examination and isolation have as yet to be overcome with this class of esters and the parent products from which they are derived, it must be obvious to the unbiased, non-speculative, reflective mind conversant with this subject and cognizant of the difficulties embraced therein, that the sum total of contributions of those who have *lived* and *worked* and *gave*, constitute but the denting or etching of the periphery of a vast sphere whose potentialities are practically limitless. Such, at least, are the views of the author.

A. Saposchnikoff[1] (see p. 1403) has shown that on continually adding sulfuric acid to nitric acid of a definite strength the vapor pressure of the HNO_3 continually increases and reaches a maximum at a point corresponding to a system $HNO_3 + n(H_2SO_4.H_2O)$. At this point the partial pressure of the HNO_3 is identical with that of anhydrous acid mixed with the same proportion of pure H_2SO_4. There is an intimate relation[2] between the vapor pressure of nitric acid in its mixtures with sulfuric acid and the nitrating capacity of such mixtures. The nitric acid used was of 1.52, 1.48 and 1.4 sp. gr.; the H_2SO_4 used 1.84 sp. gr. and one part cellulose for 100 parts of nitrating mixture. The resulting nitrocellulose was examined with regard to the amount of nitrogen it contained and to its solubility in ether-alcohol. The results represented by curves and tables were as follows: Nitric acid alone, sp. gr. 1.52, gives a nitrocellulose containing 12.06% N. Addition of 10% H_2SO_4 raises the percentage of N in the product to 13.35%. This is due to the removal of some of the higher oxides of nitrogen by the sulfuric acid which converts them into non-volatile products and thus raises the vapor pressure of the HNO_3 itself. Further addition of H_2SO_4 up to 80% has no effect upon the nitration, giving one and the same insoluble nitrocellulose with 13.2%-13.36% N. When the amount of H_2SO_4 reaches 80% the product contains 12.94% N. With a still higher percentage of H_2SO_4 nitration becomes impossible. In a mixture of 10 parts HNO_3 and 20 parts H_2SO_4 the cotton dissolves without residue and no appreciable amount of solid product can be obtained even after pouring the solution into cold water. Nitric acid, sp. gr. 1.48, used alone gives a product containing 9.05% N, while an acid of 1.4 has a very low nitrating power giving a product with only 1.4% N. The addition of H_2SO_4 to either of these acids quickly raises their nitrating capacity at the same time as through the absorption of H_2O by the H_2SO_4 the partial vapor pressure of the HNO_3 increases. When the maximum vapor pressure is reached the insoluble nitrocellulose contains the maximum amount of N 13.2%-13.4%. After reaching the maximum amount of N the product remains constant though the vapor pressure of the HNO_3 gradually diminishes through further addition of H_2SO_4. Only when the amount of H_2SO_4 reaches 80% the nitration begins to fall. This shows that the degree of nitration depends only upon the strength of the HNO_3 present in the mixture, not upon its relative amount. Changes in the temperature of the nitrating mixture have no effect upon the maximum of nitration. With a mixture containing 34% HNO_3, 61% H_2SO_4 and 5% H_2O the amount of N in the product varied only between 13.1% and 13.33% while the temperature was made to vary between +40° and —18°. Contrary to the results of Lunge and Bebie (see p. 1656) the author has never obtained a nitrocellulose containing more than 13.4% N under the conditions described above. The formation of more highly nitrated products in Lunge and Bebie's experiments was possibly due to their acid mixture having contained a larger percentage of water. The influence of water is twofold: it prevents the conversion of HNO_3 into N_2O_5 by the H_2SO_4 and furnishes a pyroxylin less liable to decomposition and loss of N during the thorough washing with water. The author is experimenting with various mixtures of the acids and water with a view to establishing whether the highest limit to nitration is represented by $C_{24}H_{18}(NO_3)_{13}O_8$. When nitric acid of various strengths is used alone the product contains 12.65% N corresponding approximately to $C_{24}H_{30}(NO_3)_{10}O_{10}$ when the acid is of sp. gr. 1.502; with the lowering of the strength of the acid the nitration falls very quickly reaching the lowest limit when there is 22.72% H_2O in the acid. The product then corresponds to $C_{24}H_{36}(NO_3)_4O_{16}$. With still weaker acids most of the cotton remains unaffected. The highest nitrating capacity is therefore possessed by anhydrous HNO_3 and the lowest by an acid corresponding to $HNO_3.H_2O$, or H_3NO_4 (orthonitric acid). As to the formation of intermediate stages of nitration we must either make the improbable assumption that there are several other hydrates of HNO_3 or suppose that the cotton itself has a tendency to form nitrates which depends upon the strength of the acid.

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[1] J. Russ. Phys. Chem. Soc. 1906, **38**, 1192; abst. C. A. 1907, **1**, 1324; J. C. S. 1907, **92**, i, 390; Chem. Zentr. 1907, **78**, I, 1185; Jahr. Chem. 1905–1908, II, 977; Seventh Int. Cong. Appl. Chem. 1909, III; abst. C. A. 1909, **3**, 2223; J. S. C. I. 1909, **28**, 747; Meyer Jahr. Chem. 1909, **19**, 333; Wag. Jahr. 1909, **55**, I, 434; Zts. Schiess. Spreng. 1909, **4**, 441, 462; J. Russ. Phys. Chem. Soc. 1914, **46**, 1102; abst. C. A. 1915, **9**, 1900; J. S. C. I. 1915, **34**, 789.

[2] A. Saposchnikoff, J. Russ. Phys. Chem. Soc. 1904, **36**, 669; abst. Chem. Centr. 1904, **75**, II, 685; J. S. C. I. 1904, **23**, 935. See J. Russ. Phys. Chem. Soc. 1900, **32**, 375; 1903, **35**, 506; Chem. Centr. 1900, **71**, II, 708; 1901, **72**, II, 1330; J. C. S. 1904, **86**, ii, 614; Bull. Soc. Chim. 1905, **34**, 1068; Rep. Chim. 1905, **5**, 186; Chem. Ztg. 1904, **28**, 574.

H. Martinsen[1] has shown by experiments with nitrobenzene that nitration in presence of concentrated sulfuric acid is a reaction of the second order, the velocity being proportional to the concentration of the nitric acid and of the substance which is being nitrated. In the present investigation the reaction was studied more closely with 6-chloronitrobenzene and 4.6-dinitro-*m*-xylene, the nitration of which proceeds much more slowly than that of nitrobenzene. Experiments were also made with other substituted benzene derivatives. In one series the nitration was carried out in presence of 95% sulfuric acid (sp. gr. 1.839 at 15°/4° C.), and in a second series, in presence of monohydrate sulfuric acid (H_2SO_4). In all cases the rate of nitration was greater with the 95% acid, and the benzene derivatives studied can be divided into two groups, according to the difference in the rates of nitration in the two media. In the case of substances of the first group, comprizing alkyl, halogen, nitro, hydroxy, and hydroxy-alkyl derivatives, of benzene, the ratio between the rate of nitration in presence of 95% sulfuric acid to that in presence of monohydrate sulfuric acid is about 3, but for substances of the second group, viz., carboxy and sulfonic derivatives of benzene, this ratio is much greater. For substances of the first group, the rate of nitration increases threefold for a rise of temperature of 10° C. (25°–35°). Addition of phosphoric anhydride to the 95% sulfuric acid has no influence on the rate of nitration. In the case of nitrobenzene, the rate of nitration falls regularly with a decrease in the water-content of the sulfuric acid between the limits $H_2SO_4.0.3H_2O$ to $H_2SO_40.4SO_3$. The influence of various substituent groups on nitration may be expressed as follows:

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[1] Zts. physik. Chem. 1905, **50**, 385; 1907, **59**, 605; abst. J. S. C. I. 1908, **27**, 139; Chem. Zentr. 1907, **78**, II, 1496; C. A. 1907, **1**, 2763; J. C. S. 1905, **88**, ii, 149; 1907, **92**, ii, 609; Meyer Jahr. Chem. 1907, **17**, 42, 163.

$$NO_2 > SO_3H > COOH > Cl < CH_3 < OCH_3 < OC_2H_5 < OH$$

The introduction of chlorine into the molecule sometimes accelerates and sometimes retards nitration. Of the other groups, that furthest to the left from chlorine retards the reaction most strongly, while that furthest to the right has the greatest accelerating action. It will be noted that compounds containing groups which have a retarding effect generally yield *m*-nitro-derivatives, while those containing groups which have an accelerating action yield mostly *o*- and *p*-nitro-derivatives.

C. Kullgren[1] has reached the conclusion that the nitric acid is only capable of nitrating when present as the compound HNO_3 and not as hydrate, the part played by the added sulfuric acid being to set free nitric acid from the hydrate. The nitric acid may be present as monohydrate in the acid mixture with even weak acid provided enough sulfuric acid is present. It was found in practice that about 3 times the amount of sulfuric acid over the nitric acid must be employed to effect a high degree of nitration, even with a relatively high water content. A. Saposchnikoff[2] has claimed the above ideas as his own.

According to E. Justin-Müller[3] two points militate against the conception of cellulose nitrate as an ester of nitric acid, one being the uncertainty as to whether cellulose possesses the characteristics of an alcohol, and the other the colloidal nature of cellulose and the fact that it can combine with varying amounts of nitric acid according to conditions. This author holds that the latter points to the assumption that the nitrocelluloses are absorption compounds,[1] and that the action of nitric acid on cellulose proceeds in two phases as follows:

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[1] Zts. Schiess. Spreng. 1908, **3**, 146; abst Wag Jahr **54**, I, 442; Jahr. Chem. 1905–1908, II, 974; Chem Zentr. 1908, **79**, I, 2024; J. C. S. 1908, **94**, i, 768; C. A. 1908, **2**, 3146; Meyer Jahr Chem 1908, **18**, 310 See F. Küster and R. Kremann, Zts anorg. Chem 1904, **41**, 1 H Erdmann, Zts. anorg. Chem. 1902, **32**, 431.

[2] Zts. Schiess Spreng. 1908, **3**, 201; abst C A. 1909, **3**, 835; Chem. Zentr. 1908, **79**, II, 231; Meyer Jahr. Chem. 1908, **18**, 310, Wag. Jahr 1908, **54**, I, 442. See also C. Kullgren, Zts. Schiess. Spreng. 1908, **3**, 146; abst. C. A. 1908, **2**, 3146.

[3] Rep. Chim. Pure Appl. 1907, **10**, 263; abst. Chem. Zentr. 1907, **78**, II, 795; Jahr. Chem. 1905–1908, II, 973. Zts. Chem. Ind Koll **2**, 49; abst. Meyer Jahr. Chem. 1907, **17**, 309; Zts. Schiess. Spreng. 1908, **3**, 415.

$$1.\ 8HNO_3 + xH_2SO_4 \longrightarrow 4N_2O_5 + 4H_2O$$

$$2.\ 2C_{12}H_{20}O_{10} + xH_2SO_4 + 4N_2O_5 \longrightarrow C_{24}H_{32}(N_2O_5)_4O_{16} + 4H_2O$$

The sulfuric acid first acts as a dehydrating agent on the nitric acid, the N_2O_5 thus formed replacing the H_2O in the cellulose molecule in the form of an absorption compound. He recommends the designation nitr*a*cellulose for the absorbed portion.

A. Müller[2] has replied to the above, and shows from the results of Vieille[3] that they are not all analogous to absorption compounds. It usually follows in the absorption of a dissolved body by another substance, the less the concentration of the dissolved substance, the greater the relative amount absorbed. The reverse of the above, however, is true in the nitration of cellulose. Vieille has attempted to show that with increasing concentration of nitration, the nitration advances, not gradually as it should in an absorption process, but by definite steps indicating compounds. To this assertion, E. Worden takes exception. Moreover, absorption processes are reversible, or if the concentration of the absorbed phase be diminished, some of the already absorbed substance will be again eliminated. Following out this line of reasoning, nitrocellulose in contact with water should give off nitric acid, even if the sulfuric acid present during nitration does aid that process by its dehydrating action as claimed by Müller. This, however, never occurs.

C. Haeussermann[4] is in agreement with J. Nef,[5] that the formation of the cellulose nitrates proceeds according to the law that when two substances react together, an addition product is first formed, and that, therefore, the esterification of cellulose proceeds in two distinctly discernible phases. They are not in accord as to whether the cellulose takes up the nitric acid in the first phase or whether the capacity of the entering oxygen exerts itself as quadri-valent, as well as the question of the actual or intimate constitutional knowledge of the cellulose nitrate configuration.

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[1] P. Zacharias, Zts. Farben. Text. Chem. **2**, 233; abst. Chem. Centr. 1903, **74**, II, 267; Meyer Jahr. Chem. 1903, **13**, 520; 1907, **17**, 309; Jahr. Chem. 1903, **56**, 1553; Wag. Jahr. 1903, **49**, II, 521.

[2] Zts. Chem. Ind. Koll. 1907, **2**, 173; abst. Meyer Jahr. Chem. 1907, **17**, 309; Chem. Zentr. 1908, **79**, I, 239; C. A. 1908, **2**, 1045.

[3] Compt. rend. 1882, **95**, 132; Mem. des poudres et salpetres, 1884-1889, **2**, 217; abst. Proc. U. S. Nav. Inst. 1882, **8**, 668; Chem. Ind. 1882, **5**, 349; Chem. Tech. Rep. 1882, **21**, II, 176; Chem. News, 1882, **46**, 66; J. C. S. 1882, **42**, 1184; Dingl. Poly. 1882, **246**, 540; Chem. Centr. 1882, **53**, 632; Bull. Soc. Chim. 1883, **39**, 527; J. S. C. I. 1882, **1**, 516; Jahr. Chem. 1882, **35**, 1187. See also Rev. Sci. 1882, **30**, 156. Arms Expl. 1898, **6**, 76; 1901, **9**, 175.

[4] Zts. Schiess. Spreng. 1908, **3**, 121; abst. Wag. Jahr. 1908, **54**, I

As a summation of the results which have been put forward, inasmuch as the cellulose molecule appears to be an aggregate in which, according to the amount of nitric acid introduced, higher or lower nitrated products result, the rational and logical viewpoint to take appears to be no other than that the change in composition goes on without a break provided the conditions are suitable, or if the esterification *does* take place in gradations, the methods of separation and identification of the products formed are not sufficiently accurate or comprehensive to admit of determining these steps with any degree of certainty. This hypothesis appears to the author as the only satisfactory explanation of the various anomalies observed and recorded by investigators of irreproachable integrity, not only in the nitration of cellulose, but also in the acetation as well. The author suggests a fruitful method of attacking this problem is the fractional precipitation of commercial nitrates in solution, in a manner somewhat similar to the purification and separation of inorganic salts by repeated crystallizations, either by deposition from saturated solutions (an impossibility with the cellulose esters), or by precipitation by adding to a solution, gradually increasing amounts of a non-solvent or non-solvent combination.

Considerable experimental proof has been adduced in support of the contention that the mixture of sulfuric and nitric acids results in the first instance in an attack on the cotton by the sulfuric acid analogous to that which goes on in the forma-

441; C. A. 1908, **3**, 3146; J. C. S. 1908, **94**, i, 768; Chem. Zentr. 1908, **79**, II, 2024; Wag. Jahr. 1908, **54**, I, 441.

5. J. A. C. S. 1904, **26**, 1549; J. C. S. 1905, **88**, i, 109; Chem. Centr. 1905, **76**, I, 337; Meyer Jahr. Chem. 1904, **14**, 368. See also D. R. P. 72969, abst. Mon. Sci. 1894, **44**, 65; Ber. 1894, **27**, 324; Zts. ang. Chem. 1894, **17**, 371.

tion of vegetable parchment, and that the nitric acid subsequently replaces the sulfuric acid in the reacting cellulose. It appears as a fact, however, that in the quartenary system, cellulose, sulfuric acid, nitric acid and water, each endeavors to carry out its *characteristic function*, the sulfuric acid to dissolve (the cellulose), the nitric acid to combine to esters, and the water to hydrate or hydrolyze, depending on the amount present in the system.

Nomenclature of the Cellulose Nitrates. As would naturally be inferred, there is no clear-cut or definite classification possible of the unknown gradations of nitrogen content in the nitration of cellulosic bodies, it being recognized in a rather loose manner that, in the technique of cellulose nitration, the highest forms of cellulose nitrates are the guncottons, esters insoluble in alcohol-ether mixtures or substantially so, but practically completely soluble in acetone.

As has been mentioned, variation in the esterification factors of acid concentration, temperature and length of immersion of the cellulose in the nitrating bath, give rise to a series of esters, often analytically indistinguishable, but readily differentiated in an approximate manner by solubility separations, and in which the nitrogen content is not indicative of the solubility, viscosity or tensile strength of the ester. Therefore, a rational classification at the present time is impossible.

1. *Guncottons.* In general, however, guncotton is the name applied to the highest forms of cellulose nitration—products containing nitrogen in excess of 13%, practically insoluble in ether-alcohol, soluble in acetone or in ethyl acetate, and but partially soluble in amyl acetate; not used in the peaceful arts. Such loose designations as "cellulose of high nitration" are of indefinite characterization and only lead to confusion.

2. *Pyrocollodions.* In the descending scale of nitrogen content from the guncotton of maximum nitration, are the pyrocollodions, products containing 12.6%–12.8% N, soluble 99%–99.5% in ether-alcohol, and produced in the United States and elsewhere as a shoulder arms powder mixed with a small amount of graphite. Soluble in ethyl acetate, acetone, diacetone alcohol and amyl acetate. Those nations whose official smokeless powder is gelatinized by ether-alcohol, manufacture a cellulose nitrate comprehended in the above, the nitrogen fluctuating within the

limits 12.5%–12.9%, usually as near to 12.7% as practicable.

3. *Pyroxylins.* The manufacture of pyroxylin lacquers, bronzing liquids, and nitrocellulose solutions intended for the protection of metal or wood, and less often for impregnation, a 12% medium flow pyroxylin is employed, readily soluble in ethyl or amyl acetates, acetone, methyl ethyl ketone, diacetone alcohol, and solutions of this class of nitrated cellulose are miscible with large amounts of non-solvents benzene or benzine without precipitation, but with considerable reduction in cost. From 11.5%–12% N are included the class of "pyroxylins"—loosely defined and with no clear-cut lines of analytical demarcation, but including the nitrocelluloses employed in artificial leather, lacquers, waterproofing solutions, bronzing liquids, nitro-artificial filaments, and the enameling and coating of hides and splits. The pyroxylins are produced in an endless number of "grades" for specific purposes, where the solubility, "flow," adhesion, ability to mix with oils, tensile strength and other factors, are modified and manipulated in the process of nitration, without at the same time varying but little the nitrogen content of the finished product. It is here, in the variation of the nitric or sulfuric acid in the nitrating bath by a fraction of 1%, by an adjustment of temperature and speed of nitration to the production of a nitrated product of pre-determined physical constants, that the nitration of cellulose rises to an *art.* And the technically useful nitrated celluloses are comprehended in the above "pyroxylin" classification.

4. *Collodions.* Next lower in nitrogen percentage that is susceptible to a definite classification, are the "collodions,"[1] containing 11.5%–12.5% N, soluble in ether-alcohol and the solvents above mentioned, soluble in wood alcohol or gelatinized by it, either dissolving partially or intumescing in ethyl alcohol. The

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[1] According to J. S. C. I. 1901, **20,** 630, collodion cotton has been defined, for the Explosive Substance Act of 1875, as follows: consists of a thoroughly purified cotton *a* of which not less than 15% is soluble in ether and alcohol, and *b*, which contains not more than 12.3% of nitrogen. Where this substance is "used or manufactured with a view to produce a practical effect by explosion" it is by Section 3 of that act an explosive in any form. But in cases where it is not intended to be used by itself as an explosive, it is not regarded as coming within the meaning of the act when it is (a) in solution in alcohol and ether, (b) wet, or (c) saturated in methylated spirit and contained in airtight cases.

In such circumstances it will not be considered as "dangerous goods" within the meaning of Section 446 of the Merchants Shipping Act, 1894. It is however regarded as an explosive when dry.

cellulose nitrates used in pharmacy, the celloidins and photoxylins employed in histological technique for imbedding, and often the photographic nitrocelluloses, are best classified under the above designation.

5. *Celluloids.* The thermoplastic pyroxylins typified by celluloid and xylonite, are of comparatively low nitrogen content, ranging from 10.6%-10.9% N, of high viscosity, great tensile strength and satisfactory solubility, in which the nitration (usually of tissue paper) is carried out at a comparatively low temperature. The camphor-inducing cellulose nitrate plastics are all of comparatively low nitrogen content, being differentiated from other cellulose nitrates used commercially, by an extremely high viscosity.

Differentiation into *nitrohydrocelluloses*, *nitrooxycelluloses*, nitrocelluloses of *high* and *low* nitration and *mean* nitrogen content have been made, but they are really meaningless. Even the above approximations are susceptible to wide modifications in special cases. Classification based upon nitrogen content alone is impossible.

It must be remembered that by judicious blending, the nitrogen content of a batch of nitrated cotton may be caused to fall into one of the above roughly designated five classes, without the product conforming to the physical properties of solubility and viscosity representative of that class. That is, the admixture of high and low nitrogen products may give a nitrocotton falling into class (2) above, but the solubility will be diminished from admixture of higher nitrated product with one of lower nitration in order to obtain a pre-determined percentage of nitrogen.

A description of a cellulose nitrate sufficiently specific for duplication must embrace: (a) statement of nitrogen content; (b) degree of solubility in a named solvent of known purity, at a temperature stated; (c) viscosity of a given weight in a specified neutral liquid of stated purity and concentration at a named temperature by a method given in detail. The omission of any one point in the above three named specifications, renders impossible the duplication of a nitrocellulose from description alone.

Commercial Designations of the Cellulose Nitrates. Made official by years of usage, the highly nitrated celluloses used primarily if not exclusively in the warlike arts are called guncotton, explosive cotton, lignia nitrica, fulminating cotton, explosive tissue and brisant cellulose. They are insoluble in ether-alcohol, but dissolve readily in acetone or ethyl acetate.

Next in order of descending nitrogen content are the pyrocollodions, soluble in ether-alcohol 95% or better, some as high as 99% soluble, and known under a variety of names as the official smokeless powders of various nations, and employed in sporting powders. These cellulose nitrates are universally colloided with a mixture of alcohol and ether, to which the various stabilizers and ant-acids have been added.

Pyroxylins, zapons, colloxylin, pyroxyle, pyroxylol, haloxylin,[1] collodolith,[2] alkolen,[3] tamidine,[4] polynitrocellulose,[5] soluble cellulose, soluble cotton wool, pyrocotton,[6] are names applied to those forms of nitrated cellulose used industrially for lacquers, waterproofing solutions, bronzing enamels, and protective coatings.

Of still lower nitrogen content, and wider range of solubility are the collodions, collodium, photocotton, negative cotton, sensitive cotton, adhesive cotton, protective cotton, ether glue, soluble fiber, crystalline,[7] filmogen,[8] hyaline,[9] krystallin,[10] vitrose,[11] celluloidine,[12] soluble guncotton—names for the cellulose esters used in pharmacy and photography. Similar is the celloidin, photoxylin, histoloid used as imbedding media in histology and pathology. Of the pharmaceutical nitrocelluloses, perlcollodion,[13] celakut, elastoskin, are ether-free collodions, in which acetone is usually the solvent, either alone or with benzene to decrease the cost (see the next topic, Pharmaceutical Nitrocelluloses).

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[1] F. P. 73110, 1866.

[2] Schippang & Wehenkel, D. R. P. 9890; abst. Wag. Jahr. 1880, **26**, 797; J. A. C. S. 1880, **2**, 303.

[3] T. Sutton, Photo. Notes, 1862, No. 144; Phot. Archiv. 1862, June, 117; Chem. Tech. Rep. 1862, **1**, I, 40.

[4] Tamidine is the nitrocellulose developed by E. Weston.

[5] Heusschen, F. P. 157728, 1883; abst. Mon. Sci. 1884, **26**, 325.

[6] Pyrocotton was proposed in 1883 by Parozzani.

[7] Year Book of Pharmacy, 1894, 227; abst. Repert d. Pharm. (3), **5**, 497.

[8] Zts. Apoth. Ver. **34**, 686, 945; abst. Year Book of Pharmacy, 1897, 252. This is an acetone solution of nitrocellulose, and is also called Collosin.

[9] "Hyaline," Le Mon. de la Photog. 1891, **30**, 28, 88.

[10] This is said to be a solution of nitrocellulose in ethyl alcohol, wood alcohol and amyl acetate.

[11] Jahr. Photog. and Reproductiontechnik, 1899, 511.

[12] Asselot, Neuste Erfind. Erfahr. 1898, **25**, 180. W. Marga, E. P. 21470, 1895; abst. Arms & Expl, 1895, **5**, 30. Ber. 1896, **29**, 324. Turpin, F. P. 189398, 1888.

[13] This is said to be an ether-free collodion manufactured by Chem. Fabr. Helfenberg.

Nitrated paper is also designated as pyropaper, paproxylin,[1] explosive paper, etheroxylin,[2] and paproxyl.[3]

The thermoplastic nitrocelluloses have been known under a multitude of names, of which celluloid, xylonite, zylonite, parkesine, fiberloid, pyraline, viscoloid, ivoryine, coralline, camphoid,[4] Arlington paste, cellonite, pyrantin, pasbosene, nitroplastic, roxylite and petrifoid, are perhaps, the most familiar.

Pharmacopeial Nitrocelluloses. The earlier investigations of nitrocellulose were along pharmacopeial lines, the "ether glue" of Schönbein, and the "sticking plaster" of Maynard and the older pharmaceutists being solutions of pyroxylin in ether-alcohol, used to coapt the edges of a wound, or constringe the surface of a denuded part. The earlier Pharmacopeias contained methods for the manufacture of the pyroxylin, and directions for obtaining the various collodions therefrom, at the same time specifying the nature and quantities of medicaments to be incorporated with the collodion. The processes of pyroxylin manufacture as devized by W. Proctor,[5] C. Mitchell,[6] E. Senft,[7] F. Luchs,[8] T. Sutton,[9] and F. Katschursky[10] are indicative of the older methods of pharmaceutical pyroxylin formation. Either the cotton was immersed in a mixture of nitric and sulfuric acid, usually for periods less than ten minutes, or the nitric acid was produced in the bath by the employment of sodium or potassium nitrates and sulfuric acid.

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[1] Cassell's Ency. Phot 1911, 392. See also Bull. de la Franc. de Phot. 1878, **24,** 70

[2] Winiwarter, E P 13935, 1852; 306. 1853. See also "Les Positifs sur Verre and Theorie et Pratique" by H Fourtoer, 1908, 12.

[3] Photo Archiv 1872, **13,** 9, 42

[4] This is a collodion substitute consisting of 1 part nitrocellulose and one part by weight of camphor and absolute alcohol, by weight.

[5] Amer. J. Pharm 1864, **36,** 304.

[6] Proc. Amer. Pharm Assoc 1874, **22,** 59; Pharm. Centralh. 1873, **31,** 267; Amer. J Pharm. 1872, **2,** 241; Bull. Soc. Chim. 1872, **18,** 373, Mon. Sci. 1874, **16,** 382; Poly. Notizbl 1873, **28,** 96; Phot. Archiv. 1873, 12; Pharm. J. Trans. (3), **2,** 1047; Chem Centr. 1872, **43,** 554; Jahr. Chem. 1872, **25,** 984; Zts. allg. Oesterr. Apotheker-Verein's, 1875; abst. Industriebl 1876, 235; Chem. Tech. Rep 1875, **14,** II, 217.

[7] Pharm. Post, 1899, 607; abst. Proc. Amer. Pharm. Assoc. 1900, **48,** 788.

[8] Dingl. Poly. 1862, **166,** 62; abst. Proc. Amer. Pharm. Assoc. 1864, **12,** 164; Poly. Centr. 1863, **29,** 270; Rep. Chim appl. 1863, **5,** 113; Poly. Notizbl. 1864, **19,** 12; Chem. Centr 1862, **33,** No. 58, Chem. Tech. Mitth. 1862–3, 36.

[9] Amer. J. Pharm. **36,** 21; abst. Proc. Amer. Pharm. 1864, **12,** 165; Rep. Chim. appl. 1862, **4,** 145; Mon. Sci. 1862, **4,** 377; Poly. Notizbl. 1863, **18,** 76; N. Jahr. Pharm. **19,** 35; Poly. Centr. 1863, **20,** 700, Jahr. Chem. 1862, **15,** 468.

[10] Pharm. Rec. 1884, 219; abst. Proc. Amer. Pharm. Assoc. 1884, **32,** 280.

The present (IX) U. S. Pharmacopeia quite rightly refrains from including directions for the manufacture of pyroxylin, for the mechanical and practical equipment of the usual druggist is not such as to produce with profit this highly specialized product, proper manufacture of which is an art—almost a *fine* art—to which statement G. Brown[1] does not agree.

The 1890 U. S. Pharmacopeia gave the following formula for pyroxylin manufacture, which yields results, quite satisfactory for small scale production. The formula directs to use 100 gm. purified cotton, 1400 cc. nitric acid, and 2200 cc. sulfuric acid, the acids being mixed in a glass or porcelain vessel, cooled to 32°, and the cotton added. The cotton is "imbued" with the acid thoroughly by means of a glass rod, the mixture allowed to macerate until a sample withdrawn, washed with water, then alcohol, is found to be soluble in a mixture of 1 vol. alcohol and 3 vols. ether. The nitrated cotton is then removed from the bath, washed first with cold, then with hot water until neutral, "dehydrate" and dry it in "small, detached pellets," by means of a water or steam bath at a temperature not exceeding 60°.

The British Pharmacopeia of 1914 contains the following directions: Take 10 gm. cotton and 50 cc. each nitric and sulfuric acids, mixing the latter in a porcelain mortar. Immerse the cotton in this mixture, and after it has been thoroughly wetted by the acids, stir it for 3 minutes with a glass rod; transfer it to distilled water, wash until free from acid, drain, and dry the pyroxylin in a warm room. Prepared in the above manner, the pyroxylin should be "readily soluble in a mixture of equal volumes of 90% alcohol and ether—distinction from guncotton." Notice that no temperature of nitration is specified.

The French Codex has a somewhat similar formula, but different proportions. It directs the maceration of 55 parts of well-dried cotton in a mixture of 1000 parts sulfuric acid, sp. gr. 1.84, and 500 parts nitric acid, sp. gr. 1.42, which has been cooled to 30°. The German Pharmacopeia directs a mixture of 1000 parts sulfuric acid sp. gr. 1.83, and 400 parts nitric acid, sp. gr. 1.38, into which, when cooled to 20°, is immersed 55 parts purified cotton, the cotton to be macerated in the mixture for 24 hours at 15°-20°.

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[1] Proc. Louisiana Pharm. Assoc. 1909, 66. See Amer. J. Pharm. 1861, **33**, 316. Archiv. Pharm., Dec. 1861; abst. Drug. Circ., April 1861; Amer. J. Pharm. 1861, **33**, 222. Amat. Phot. 1897, **25**, 215, 225; 1899, **30**, 258.

According to J. van der Marck,[1] whereas the Dutch Pharmacopeia recommends nitration at approximately 20° with a mixture of 17.5% nitric acid, 67.85% sulfuric acid, and 14.65% water, better results may be obtained at approximately 15° with 16% nitric acid, 65% sulfuric acid, and 19% water, there being used 30 parts by weight of nitrating acid to one of cotton. Methods of pyroxylin formation as directed by the Pharmacopeias may be found in "Nitrocellulose Industry," E. Worden, 1911, **1**, 114.

The official description for pyroxylinum of the U. S. Pharmacopeia IX, is as follows: "A product obtained by the action of a mixture of nitric and sulfuric acids on cotton and consisting chiefly of cellulose tetranitrate ($C_{12}H_{16}(ONO_2)_4O_6$ = 504.17). Preserve it in cartons, packed loosely and protected from light and moisture."

The Pharmacopeias describe pyroxylin as a yellowish white, matted mass of filaments, resembling raw cotton in appearance, harsh to the touch, exceedingly inflammable, burning very rapidly when unconfined with a luminous flame, and less explosive than cellulose trinitrate (i. e., guncotton). Slowly but completely soluble in 25 parts of a mixture of 3 volumes ether and 1 volume alcohol. Soluble in acetone and in glacial acetic acid, and precipitated from these solutions on the addition of water. It should leave no weighable residue of mineral impurities when ignited. When kept in well-closed bottles and exposed to the light, it is decomposed with the evolution of nitrous vapors, a carbonaceous mass being deposited.

In Germany, the name "pyroxylin," which in England and the United States is used to designate those soluble cellulose nitrates used in the manufacture of collodion and lacquers, is usually restricted to the insoluble and explosive variety better known as guncotton; the name colloxylin being there given to the more soluble nitric esters corresponding to our collodions.

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[1] Pharm Weekblad. 1917, **54**, 53; abst. C. A. 1917, **11**, 1518.

In the various methods for manufacturing collodion especially adaptable for pharmaceutical uses, i. e., maximum adhesion, tensile strength, suppleness and stability, especial emphasis is placed on so conducting the esterification process that an absolutely complete solubility in ether-alcohol admixture will result, but little attention has apparently been directed to so manipulating the nitrating constants, that an ester of minimum viscosity will result. Furthermore, it is a doubtful point whether a completely soluble pyroxylin will give the maximum adhesiveness, it having been repeatedly shown that the small number of filaments which are present in unfiltered collodions, actually assist adhesion by the binding nature of the partially dissolved filaments. The question of nitration to a maximum contractility in solution, is also another point which pharmacists apparently have devoted but little attention. These points, however, have been taken into consideration by the manufacturers of various proprietary collodions (see Chapter XII) with the result that in many instances the proprietary collodions are superior to those prepared according to the pharmacopeial directions.

Pertinent comments on pharmaceutical pyroxylins have been made by T. Tyrer,[1] T. Schlumberger,[2] R. Breves,[3] L. Brown,[4] A. Schamelhout,[5] and others, to the original references of which the reader is referred.

Properties of the Cellulose Nitrates. It is not possible to distinguish cotton from nitrated cotton or the various cellulose nitrates among themselves by visual inspection alone. Without taste or smell, nitrocellulose preserves perfectly the appearance of the cotton from which it is prepared, being, however, harsher to the touch, and emitting a slight crackling sound when compressed. When rubbed, especially at a moderately warm temperature, its fibers become strongly electrified, and will adhere to the hand.[1] This property diminishes with decreasing N per cent.

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[1] Chem. and Drug. 1896, 207; Pharm. J. 1896, 109; J. S. C. I. 1896, **15**, 672.

[2] Pharm. Centralh. 1896, **38**, 772; Pharm. J. 1898, Jan. 24. See also E. Bronnert and T. Schlumberger (E. P. 1858, 1896; abst. J. S. C. I. 1897, **16**, 355) for the manufacture of pyroxylin suitable for collodion.

[3] Pract. Drug. 1910, **28**, 39.

[4] Bull. 150, Kentucky Agric. Exper. Sta. 1910, 143.

[5] Bull. Soc. Roy. Pharm. Brux. 1909, **53**, 75. For report by Belgian Inspectors of Pharmacies see J. d. Pharm. d'Anvers, 1909, **65**, 588.

Pure nitrocotton is substantially white in color, but commercial varieties have usually a slight yellow tint, especially noticeable when in the wet state. This is due to the fact that raw cotton as used for nitration contains some coloring matter, and this pigment or its derivatives is not wholly removed in the process of nitration or subsequent purification. Sliver cotton results in the formation of a more nearly white final product than is given with cotton waste. When nitrocotton is stored under water or in diffused light, it is slowly bleached. A more rapid bleaching may be brought about by peroxide or chlorine bleaching after nitration, and this method is sometimes resorted to with nitrated paper intended for transparent sheets of plastic. Pure nitrocellulose also resembles cotton in being neutral.

Since it is practically impossible to distinguish cotton from nitrocotton by inspection, it has been proposed[2] to dye the latter, which does not affect the stability. A difference may be detected between the nitrated and un-nitrated product upon microscopical examination in polarized light, as well as in electrical properties (see p. 1766). Unlike cotton, the nitrated product is soluble in acetone and many other solvents, from which the product may be precipitated *unchanged*. When wet guncotton is treated with an aqueous solution of iodine in potassium iodide and subsequently moistened with dilute sulfuric acid, a yellow color is obtained, while under similar treatment, cotton is colored blue.[3] Under other tests a marked difference appears, such as when exposed to the action of heat. While in general, cotton is chemically inert, guncotton shows the properties of a cellulose ester.[4]

E. Sarrau and P. Vieille[5] have obtained the heat of formation

[1] Plates for static electric machines have been constructed by dissolving nitrated cellulose, forming large sheets or films and pressing these together into a plate, after which they are cut or sawed into the desired shape and thickness. R. Fortun and E. Semprun (E. P. 8280, 1901; abst. J. S. C. I. 1901, **20**, 777) have devized a process for making separators for use in secondary galvanic batteries, by superficially nitrating sheet cardboard, and applying a coat of silicate paint to the dried surfaces.

[2] J. Bonjean, Compt. rend. 1847, **24**, 22; abst. Berz. Jahr. 1849. **28**, 351; Annuaire de Chim. 1847, **3**, 454; Jahr. Chem. 1847-8, **1**, 1145.

[3] G. Kindt, Pogg. Ann. 1847, **70**, 967; abst. Dingl. Poly. 1847, **103**, 214; Jahr. Chem. 1847-8, **1**, 1137; Berz. Jahr. Chem. 1848, **29**, 351; Liebig-Kopp. Ann. Rep. 1847-8, **2**, 370.

[4] T. Bokorny, Chem. Ztg. 1896, **20**, 986; abst. Jahr. Chem. 1896, **49**, 1030; Chem. Centr. 1897, **68**, I, 30.

[5] Bull. Soc. Chim. 1880, **33**, 581; abst. Jahr. Chem. 1880, **33**, 127;

and of transformation of guncotton, the experiments being made with a mixture of the di- and tri-nitrated derivatives. The heat of transformation of one equivalent weight of guncotton was found to equal 1070 calories, and the heat of formation, 542 calories. B. Oddo has recently determined[1] that cellulose absorbs gases to extents increasing with the solubilities of the gases in water (see p. 529) and absorption of a second gas is accompanied by partial displacement of a gas already absorbed. Both deca- and endeca-nitrated celluloses absorb dry hydrogen chloride and sulfur dioxide. After a time, however, red vapors are emitted, and even after being kept in an evacuated space, the product contains ionic chlorine and small proportions of nitrogen. The volume of SO_2 absorbed by nitrated cellulose (13.32% N) is about five times that absorbed by an equal weight of cellulose.

L. Vanino has shown[2] that if dry guncotton is impregnated with sodium peroxide and a few drops of water then added, the guncotton is immediately ignited but not detonated. It is necessary to avoid excess of water. The addition of a small amount of formaldehyde to the water apparently accelerates the reaction considerably. If to ordinary commercial formalin a small quantity of sodium peroxide be added, a violent detonation occurs, with destruction of the glass vessel. When the peroxide is added in too small amounts only small sparks of flame appear, unaccompanied by an explosion, or only a development of gas is observed. With larger proportions, however, the explosion occurs regularly, with a dull report.

Whereas in the alkaline saponification of organic nitrates there are usually obtained dark colored resin-like bodies, primarily derived from the alkyl complex of the nitrate, T. Carlson has found[3] that with the nitrates of the polyatomic alcohols the con-

Chem. News, 1880, **42**, 282; J. A. C. S. 1880, **2**, 435; J. C. S. 1881, **40**, 342; Ber. 1880, **13**, 1477.

[1] Gazz. chim. ital. 1919, **49**, II, 127; abst. J. S. C. I. 1920, **39**, 12-A; C. A. 1920, **14**, 1529. The absorption of SO_2 by 1 gm. nitrocellulose in three experiments, was 12.60%, 12.97% and 12.39%, respectively.

[2] Zts. ang. Chem. 1902, **15**, 1299; abst. J. S. C. I. 1903, **22**, 49; Chem. News, 1903, **88**, 257; J. C. S. 1903, **84**, i, 67, 232; Bull. Soc. Chim. 1903, **30**, 637; Rep. Chim. 1902, **2**, 46; Chem. Centr. 1902, **73**, II, 1499; 1903, **74**, I, 265; Chem. Ztg. Rep. 1902, **26**, 354; Jahr. Chem. 1902, **55**, 978, 1055; Zts. anal. Chem. 1902, **41**, 619.

[3] Arkiv. f. Kemi. Min. Geol. 2, No. 26; 3, No. 7, 8; Ber. 1906, **39**, 2752; 1907, **40**, 4191; Chem. Centr. 1906, **77**, II, 1481; 1907. **78**, II, 1226, 2033, 2034; 1908, **79**, I, 934.

version proceeds significantly more rapid. For instance, nitroglycerol saponifies as alkali nitrate, 67%; glycol nitrate a s alkali nitrate, 87%; and nitrocellulose (12.5% N) to about 82%. Here the alkyl complex became more or less completely destroyed, and the alcohol was not at all, or only in traces regenerated.

C. Munroe[1] exploded wet guncotton in moist sea sand which still retained some salt. The grenade in which the nitrocellulose had been placed was ruptured into only a few pieces, and the surrounding sand was partly sintered in spots. The pieces which had been melted were glazed on the inner side with a sort of gray glaze, not over 1 mm. thick.

Stability of the Cellulose Nitrates. The general subject of stability has been subdivided in this volume under five headings as follows:

1. In the *historical development* of the art (pp. 1567-1635) as indicating the importance which investigation on stability played in the development of this subject, if not actually saving it from extinction.

2. The *theoretical considerations* involved in the general subject of the proneness to decomposition of the nitrocelluloses and the underlying principles connected therewith, comprizing the subject matter of the present topic.

3. The *manipulative details* in stabilization incident to actual production of the cellulose nitrates as in the boiling (p. 2071), beating (p. 2083), poaching (p. 2098), and blending (p. 2107) operations described in the next chapter.

4. The various *tests* and quantitative methods whereby the relative stability of the product is determined, as detailed in Chapter XI of this volume.

5. Incidental mention of the more prominent of the *stabilizers*, ant-acids, activators, accelerators, and other liquid and solid bodies which have been proposed from time to time for increasing the stability of the nitrocelluloses, or rather, for prolonging the period in which their decomposition constitutes an element of danger, are given in Chapter XII in synopsis only, their general discussion and elaboration constituting a section in Volume II.

One who has understandingly read the historical development of the cellulose nitrates as recorded in the first portion of this chapter, must have been impressed with the vital nature of the subject of stability as contributing to advancement, for it is true that in the earlier days of the history of this art, real advancement seemed to occur only at these periods when notable methods of increasing stability and diminishing the perceptible rate of decomposition were disclosed. And it is not far-fetched to say that no problem connected with modern explosives is of more importance or more elusive than that of the stability of the nitric esters of cellulose. Whereas black powder and similar inorganic nitrate combinations may be stored indefinitely under dry conditions without serious deterioration; and while the aromatic nitro-compounds as picric acid and trinitrotoluene may be preserved for comparatively long periods without perceptible decomposition; nitrocellulose and nitroglycerol, on the other hand, have a measurable rate of decomposition when stored under ordinary atmospheric conditions, which increment of decomposition is materially augmented with rise of temperature.

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[1] Amer. J. Sci. 1917, (4), **43**, 389; abst. Chem. Zentr. 1918, **89**, I, 962; C. A. 1917, **11**, 2043; J. S. C. I. 1907, **36**, 669.

It will be remembered that v. Lenk sought to increase stability by boiling with dilute alkali and then adding water glass (pp. 1593–1598); F. Abel comminuted the nitrocotton (pp. 1599–1616), while M. Bonet,[1] S. de Luca,[2] A. Hardwich,[3] J. Nickles,[4] A. Hofmann,[5] A. Davanne,[6] F. Hess,[7] and others,[8] made various suggestions.

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[1] Compt. rend. 1861, **53**, 405; abst Dingl Poly. 1861, **162**, 137, J. prakt. Chem. 1862, **85**, 380, Rep Chim Pure, 1862, **4**, 15, Jahr. Chem. 1861, **14**, 712; Poly. Centr 1861, **27**, 1519, Mon Sci. 1861, **3**, 510.

[2] Compt. rend. 1861, **53**, 298, Instit 1861, 275, Dingl Poly. 1861, **162**, 135; J. prakt. Chem. 1862, **85**, 378, J. Pharm. (3), **41**, 483; Jahr. Chem. 1861, **14**, 713; Poly. Centr. 1862, **28**, 221

[3] Lond. Photog. J.; abst. Rep. chim appl. 1860, **2**, 65; Jahr. Chem. 1860, **13**, 499. In this connection see C Rand, Amer. J Pharm. 1849, **21**, 209, 212.

[4] Mem. Acad. Stanislas, 1861, 126, J de Pharm. 1861, **39**, 116, 158; **40**, 277; Jahr. Chem. 1860, **13**, 499.

[5] J. C. S. 1860, **13**, 76; Ann. 1860, **115**, 282; abst. Chem. Centr. 1860, **31**, 976; Rep. chim. appl. 1861, **3**, 119; Jahr: Chem. 1860, **13**, 499, Dingl. Poly. 1860, **158**, 237; Mon. Sci. 1864, **12**, 137.

[6] Rep. chim. appl. 1860, **2**, 65; abst. Jahr. Chem. 1860, **13**, 499. Anon., Zts. Schiess. Spreng. 1912, **7**, 370; abst. C. A. 1913, **7**, 701.

[7] Mitth. Art. Genie-Wesens, 1876; abst. Dingl. Poly. 1876, **221**, 548; Chem. Tech. Rep. 1876, **15**, 389; Wag. Jahr. 1876, **22**, 496; Indbl. 1876, 274; Zts. Chem. Grossgew. 1876, **1**, 230. Cf Dingl. Poly. 1875, **218**, 227. Mitt. Art. Genie-Wesens. 1879; abst. Dingl. Poly. 1879, **234**, 43; Wag. Jahr. 1879, **25**, 398.

[8] Poly. Centr. 1849, **15**, 1467. J. C. S. 1868, **20**, 522, 538, 561.

F. Abel,[1] in his several attempts to purify and stabilize cotton, was of the opinion that the lower and more soluble nitrates were what caused the instability, and this was apparently experimentally demonstrated by dissolving out the lower esters whereby the more insoluble portions which remained were found to possess a higher stability, but there is nothing in his writings to show that it occurred to him that, in dissolving out the lower esters he was at the same time removing the sulfuric containing esters, and it was to the presence of these that the instability, in a great measure was due.

E. Schunk in 1868 made a good point which apparently has escaped general observation.[2] In his investigation of the composition of cotton wax (see p. 534). Whereas the generally accepted opinion at that time was that the wax and hygroscopic normal impurities in cotton cellulose was the cause of the instability in the nitrated product, Schunck isolated and nitrated these bodies, and found that explosive compounds were not formed. E. Divers found[3] soluble pyroxylin made from Swedish filter paper when exposed to diffused daylight at the end of several years, emitted red fumes and left gummy or pectin-like products. Wallis[4] found that properly prepared collodion cotton will keep unchanged for many years when immersed in ethyl alcohol. C. Curtis and A. Durnford[5] added chalk as a neutralizant to the finished preparation, a practice which has been carried out to the present day in England, notwithstanding many criticisms of the practice as will be discussed herein later. A. Luck and C. Cross[6] preferred to stabilize cellulose nitrate by the addition of a concentrated solution of lead acetate or zinc chloride.

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[1] Phil. Trans. 1867, **157**, 181; abst. J. C. S. 1867, **5**, 505; Proc. Roy. Soc. 1867, **16**, 417; Phil. Mag. 1867, (4), **33**, 544; Sill, Amer. J. Sci. 1867, (2), **44**, 288; Chem. News, 1867, **15**, 203; Bull. Soc. Chim. 1867, (2), **7**, 527; Jahr. Chem. 1867, **20**, 912.

[2] Men. Man. Lit. and Phil. Soc. 1868, (3), **4**, 95; Chem. News, 1868, **17**, 118; 1874, **29**, 5; Bull. Soc. Chim. 1868, **10**, 70; Chem. Centr. 1868, **39**, 113; 1869, **40**, 112; Jahr. Chem. 1868, **21**, 980; Wag. Jahr. 1868, **14**, 614; Poly. Centr. 1868, **34**, 1006; Dingl. Poly. 1868, **188**, 496; Schwiez. Poly. Zts. 1868, 121; J. de Pharm. (4), **8**, 232; Deut. Ind. Ztg. 1868, 252.

[3] J. C. S. 1863, **1**, 91; abst. Chem. News, 1863, **7**, 154; Zts. Chem. Pharm. 1863, 237; J. prakt. Chem. 1864, **91**, 58; Chem. Centr. **34**, 690; Bull. Soc. Chim. 1864, **1**, 46; Jahr. Chem. 1863, **16**, 569.

[4] Wieck. Gewerbztg. 1860, No. 40; abst. Poly. Centr. 1864, **30**, 1590; Chem. Tech. Rep. 1864, **3**, II, 106.

[5] E. P. 12591, 1899; abst. J. S. C. I. 1900, **19**, 689. See P. Allyre, F. P. 443555, add. 16836, 1912; abst. C. A. 1913, **7**, 1291; Mon. Sci. 1913, **79**, 186; Chem. Ztg. Rep. 1913, **37**, 36.

[6] E. P. 18868, 1898; abst. Mon. Sci. 1900, **56**, 131; Chem. Ztg. Rep.

C. Hoitsema has shown[1] that if guncotton be subjected to very gentle heating in vacuo it is gradually decomposed into a black residue and gaseous product, consisting at the beginning, of a small quantity of higher nitrogen oxides, but later on, of nothing but nitrogen and nitric oxide. In a later research[2] it was determined that the unstable bodies in guncotton give rise to the higher oxides of nitrogen, while stable guncotton yields only nitrogen and nitric oxide. On these grounds he has designed an apparatus for determining the stability consisting of two glass-stoppered U-tubes connected together, in the first of which is placed the guncotton, the second containing glass wool moistened with diphenylamine in sulfuric acid. The tube containing the guncotton is then placed in an oil bath for a specified period, during which time dry CO_2 is aspirated through, when it will be found that the diphenylamine has developed the blue color due to the presence of higher nitrogen oxides. The process is repeated at succeeding lower temperatures until a point is reached where no blue coloration is produced, and this temperature taken as the indication of stability. The following comparison with the Abel test and the method of J. Simon-Thomas[3] gives the comparative results (see p. 1704).

In the decade 1901–1910 appeared a large number of important contributions to the general subject of the instability of cellulose nitrate, from which in their entirety permit of drawing a number of useful generalizations. In 1905 A. Cocking and Kynoch, Ltd., were granted patent protection for the use of barium and potassium acetates, citrates, oxalates, and tartrates

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1900, **24**, 20; Arms Expl. 1899, **7**, 131. E. P. 24662, 1898; abst. Arms Expl. 1900, **8**, 70; J. S. C. I. 1898, **17**, 1214; 1899, **18**, 296; 1900, **19**, 375.

[1] Zts. physik. Chem. 1896, **21**, 137; abst. Wag. Jahr. 1897, **43**, 485; Ber. 1896, **29R**, 1067; Chem. Centr. 1896, **67**, II, 987, 988; J. C. S. 1897, **72**, ii, 17. Zts. physik. Chem. 1898, **27**, 567; abst. Jahr. Chem. 1898, **51**, 381; Chem. Centr. 1899, **70**, I, 460.

[2] Zts. ang. Chem. 1899, **12**, 705; abst. J. S. C. I. 1899, **18**, 857; Chem. Centr. 1899, **70**, II, 547; Jahr. Chem. 1899, **52**, 1304; Mon. Sci. 1899, **53**, 826; Tech. Chem. Jahr. 1899, **22**, 146; Meyer Jahr. Chem. 1899, **9**, 300; Wag. Jahr. 1899, **45**, 423.

[3] Zts. ang. Chem. 1898, **11**, 1003, 1027; 1899, **12**, 55; abst. J. S. C. I. 1898, **17**, 1179, 1180; 1899, **18**, 174; Mon. Sci. 1899, **53**, 145, 372; Chem. Centr. 1899, **70**, I, 76, 509; 1899, **70**, II, 219; Jahr. Chem. 1898, **51**, 1379; Meyer Jahr. Chem. 1898, **8**, 327; Wag. Jahr. 1898, **44**, 382; Rev. Intern fals. 1899, **12**, 82. Zts. ang. Chem. 1907, **20**, 1143; abst. J. S. C. I, 1907 **26**, 840; Chem. Zentr. 1907, **78**, II, 955,

as combined stabilizers and inflammability reducing additions to guncotton;[1] C. Duttenhofer brought forth the use of alkali bicarbonate for the same purpose,[2] oxalic acid and oxalates[3] having also been proposed.

Sample	Abel's Test Minutes	Thomas' Test Days	Hoitsema's Test °C
Guncotton (Stowmarket)...	4	9-11	100
Guncotton (Walsrode)...	33-39	10-10½	100
Guncotton (Kruppamühle).	12	5	100
Flake-powder (Muiden)...	35	6-8	80
Flake-powder (Cöln-Rottweil).	7-9	8-8½	80
Ballistite (Muiden)	23-27	6½-8	70
Ballistite (Düneberg) ...	13	5½-6 Hours	80
Cylinder-powder (Muiden)...	48	5½ Days	90
Cylinder-powder (Düneberg) .	60	7-8	90

In 1902 appeared the results of the investigations of W. Will[4] on the stability of nitrocellulose, in which he heated 10 gm. of a normal nitrocellulose at 135° in a current of CO_2 as described in Chapter XI, the nitrogen evolved being collected and measured. The amount of water formed also was determined by passing through a calcium chloride tube, and at definite periods the total loss in weight was determined by weighing the residue. After 371 hours no further loss in weight was obtained by continued heating, when it was found that the residue weighed 3.3 gm., and contained 0.170 gm. nitrogen, the original 10 gm. nitrocellulose containing 1.310 gm. N. The ratio between the total loss of weight and the amount of nitrogen separated remained throughout the experiment at about 100:18.5. The ratio between the amount of water and nitrogen was about 1.9:1. The ultimate composition of the residue was C, 44.4; H, 2.14; N, 5.3; O, 47.9%.

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[1] E. P. 15564, 15565, 15566, 1905, abst. J. S. C. I. 1906, **25,** 497, 609; Chem. Ztg. Rep. 1906, **30,** 487; Zts. Schiess. Spreng. 1906, **1,** 262; Arms Expl. 1906, **14,** 82, 93.

[2] E. P. 24782, 1904, abst. J. S. C. I. 1905, **24,** 105; Mon. Sci. 1907, **67,** 107; Chem. Ztg. Rep. 1906, **30,** 254; Meyer Jahr. Chem. 1905, **15,** 359. F. P. 364413, 1906; add. 6620, 7749; abst. J. S. C. I. 1906, **25,** 911; 1907, **26,** 167.

[3] "The Flameless Explosives Co.," Ltd., Wag. Jahr. 1888, **34,** 498. Cf. W. Scott, Breslauer Gewerbl. 1866; abst. Chem. Tech Rep. 1866, **5,** I, 102.

[4] Zts. ang. Chem. 1901, **14,** 743, 744, 783; abst. J. S. C. I. 1901, **20,** 932; 1902, **21,** 1470, 1554, 1555; Chem. Centr. 1901, **72,** II, 606, 667; Jahr. Chem. 1901, **54,** 894; Meyer Jahr. Chem. 1901, **11,** 316; 1904, **14,** 369; Tech. Chem. Jahr. 1901, **24,** 204; Wag. Jahr. 1901, **47,** I, 501. Mitt. Centralstelle Wissensch. Techn. Untersuch. 1900, **5,** 1902, (3), 30; abst. J. S. C. I. 1901, **20,** 609; 1902, **21,** 1554.

Based on these and other considerations, the author concludes that the nitrocellulose is mainly decomposed according to the equation:

$$C_{12}H_{15}(NO_2)_5O_{10} = C_{10}H_3NO_8 + 4NO + 6H_2O + 2CO$$

which would require a ratio between total loss of weight and amount of nitrogen separated of 100·19.7, and between the amount of water evolved and that of nitrogen of 1.9: 1. Besides nitric oxide, water and carbon monoxide, it is probable that, owing to side reactions, nitrogen, carbon dioxide and possibly nitrous oxide are formed. The fact that by prolonged heating at 135° the whole of the nitrogen is not evolved from nitrocellulose, points to a secondary action of the separated oxygen compounds of nitrogen on the nitrocellulose. This quantitative stability test is an important contribution to the means at the disposal of the investigator in forming a judgment as to the relative keeping qualities of nitrocellulose.

R. Robertson[1] has subjected the method and conclusions of Will to a searching analysis, and has added several refinements to the method, (see Chapter XI).

A. Leroux,[2] in discussing the influence of nitric and sulfuric acids on nitroglycerol and nitrocellulose explosives, makes the (rather surprising) statement that the supposed dangerous effect of free acid on these explosives is a fallacy, being based entirely upon assumption without any experimental evidence.

A. Voigt truly maintains[3] that nitrocellulose for celluloid and pyroxylin lacquer manufacture should be as carefully stabilized as if intended for warlike purposes; W. Normann[4] and B. Schreiber[5] dilate on the proneness to auto-combustion of pyroxylin plastics, to which K. Voigt[6] properly takes exception.

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[1] J. S. C. I. 1902, **21**, 819; abst. Mon. Sci. 1903, **59**, 658; Jahr. Chem. 1902, **55**, 1055; Chem. Centr. 1902, **73**, II, 540. J. C. S. 1907, **91**, 761; abst. C. A. 1907, **1**, 1772, J. S. C I. 1907, **26**, 638; Chem. Zentr. 1907, **78**, II, 95; Wag. Jahr. 1907, **53**, I, 438.

[2] Cong. de Chimie et Pharm. Liege, July, 1905; Bull. Soc. Chim. Belg. 1905, **19**, 243; J. S. C. I. 1906, **25**, 234; Wag. Jahr. 1906, **52**, I, 496; Zts. Schiess. Spreng. 1906, **1**, 179, 218.

[3] Zts. ang. Chem. 1908, **18**, 1800; abst. Wag. Jahr. 1905, **51**, II, 572 See also Zts. ang. Chem. 1906, **19**, 237, 286; Mon. Sci. 1907, **66**, 190.

[4] Chem. Ztg. 1905, **29**, 94, 128; abst. Wag. Jahr. 1905, **51**, II, 572.

[5] Chem. Ztg. 1905, **29**, 85, 128; abst. Wag. Jahr. 1905, **51**, II, 572.

[6] Chem. Ztg. 1905, **29**, 188; abst. Wag. Jahr. 1905, **51**, II, 572; Zts ang. Chem. 1905, **18**, 2300.

A peculiar observation has been recorded by L. Vanino,[1] he having found that when guncotton is treated with 20% solution of formaldehyde and allowed to dry, it loses its sensitiveness to explosion by percussion, but on removing the paraform deposited on the nitrocellulose by boiling with water, or mechanically by beating, it resumes its ordinary explosive properties. No effects of decomposition are said to be observable by this treatment.

Kismiemsky[2] has made use of the facts given by Will regarding the stability of nitrocelluloses prepared from different acid mixtures and with varying amounts of purification. Will's method for determining stability consists in noting the loss of nitrogen from 2.5 gm. of nitrocellulose at a temperature of 135°. Results are expressed as curves, using as coördinates the time of heating and the loss of nitrogen in mgrms. The composition of any mixed acid is represented by the formula, $2HNO_3 + aH_2SO_4 + bH_2O$. Thus, in the notation used (4-1/1) represents the following acid mixture: $2HNO_3 + 1.3H_2SO_4 + 0.6H_2O$; that is, H_2O 4%, H_2SO_4 48%, HNO_3 48%. The "strength" of a mixed acid is expressed by the value (a — b). From curves showing the loss of nitrogen on 2.5 gm. of nitrocellulose at 135°, it is found that the stability increases as the strength of (a — b) of the acid mixture decreases. (1st Law.) It is shown that nitrocelluloses prepared from acids, for which $(a - b) > 0$ do not reach their "limit state" of stability after even 100 hours' boiling, while those prepared from weaker acids attain their "limit state" after 30 hours; that is, the value of N_{135} is constant after 30 hours' boiling. For all nitrocelluloses in the "limit state" it was found that the loss of nitrogen is directly proportional to the time of heating at 135°. (2nd Law.) The value N_{135} expresses the loss of nitrogen in mgrms. from a 2.5 gm. sample during 15 min. heating at 135°. From a series of determinations on nitrocelluloses prepared from acid mixtures with varying values of (a — b), a value for N_{135} is found as follows: $N_{135} = 0.41 + 0.1(a - b)$. (1) The 1st law given above is verified by the following values for the nitrocelluloses investigated:

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[1] Ber. 1901, **34**, 1128; abst. J. S. C. I. 1901, **20**, 747; Chem. Centr. 1901, **72**, I, 1196; Chem. Tech. Rep. 1901, **40**, 236; Chem. Ztg. Rep. 1901, **25**, 161; Jahr. Chem. 1901, **54**, 896; Tech. Chem. Jahr. 1901, **24**, 208. Zts. ang. Chem. 1902, **15**, 1299; abst. J. S. C. I. 1903, **22**, 49; Chem. Centr. 1903, **74**, I, 265; Jahr. Chem. 1902, **55**, 1055; Tech. Chem. Jahr. 1903, **26**, 167.

[2] Mem. poudres. 1899–1900, **10**, 64; 1905–1906, **13**, 247; J. Art. Russ. 1904, No. 9; abst. J. S. C. I. 1907, **26**, 892; Meyer Jahr. Chem. 1900, **10**, 321; 1901, **11**, 316; Zts. ang. Chem. 1900, **13**, 965.

Designation of Acid Mixture	(a — b)	N_{135} Calculated	Experimental
(4—3/1)	+2.7	0.68	0.62
(9—3/1)	+1.1	0 52	0.54
(14—3/1)	—0.7	0.34	0.35
(14—1/1)	—1.0	0.31	0.29
(19—1/1)	—2.0	0.21	0.16
(19—3/1)	—2.7	0.14	0.13

For temperatures other than 135° the same relation holds true, as the following table of tests of a nitrocellulose shows:

Values of N*t* for Varying Temperatures

	N*t* Calculated			N*t* Calculated	
t°	Experimental		t°	Experimental	
126.5	0.2	0.18	147 0	2.5	2.70
129.5	0.3	0.25	149 0	3.4	4.10
133.5	0.4	0.38	151.0	4 5	5.10
137.0	0.7	0.67	153 0	5 9	5 46
139.0	0.9	0.87	155.0	7.7	6.70
141.0	1.3	1.52	157.0	10.0	10.05
143.0	1.5	1.65			

The author derives a value for Nt as follows: $D_1 = Dt\ qt{-}t_1$, (formula of Guttmann), where t and t_1 = temperature of heating, Dt and Dt_1 = time of heating at given temperature to produce a given loss, q = index of progression of the stability of the sample. Also $4Nt\,Dt$ = loss of nitrogen in Dt hours, and $\frac{Nt}{N_{135}} = \frac{D_{135}}{Dt}$, but $\frac{D_{135}}{Dt} = qt^{135}$ $\therefore N = Nt_{135}\,qt^{-135}$. From an average of the results in the table, the value for q is found to be 1.144, and substituting the value of N_{135}(1), then $Nt = [0.41 + 0.1(a - b)]$ $(1.144)t^{-135}$ (2). A series of values for Nt obtained experimentally by Will at temperatures from 135°-160° on two different samples of nitrocellulose, are calculated from the formula (2) by the author and agree closely with the experimentally obtained values.

O. Silberrad and R. Farmer,[1] in studying the stability of nitrocellulose, examined 800 kilos of a gelatinized nitrocellulose stored in a magazine which was maintained at a constant temperature of 54.4° by means of steam pipes, steam being also blown directly into the chamber in order to supply enough moisture to facilitate hydrolysis of the nitric ester. After 23 weeks it was found that the tubes of nitrocellulose were in many instances filled with a crystalline deposit of oxalic acid. 100 kilos of the explosive were now heated to 80° with an equal weight of water, and the solution filtered. The residue consisted of practically unaltered nitrocellulose. In the aqueous solution the presence of nitrous and nitric acids, ethyl nitrate and nitrite, excess of alcohol, ammonia, and also formic, acetic, butyric, dihydroxybutyric, oxalic, tartaric, isosaccharinic, and hydroxypyruvic acids, were detected. In another portion of the aqueous solution, after neutralizing, and distilling off the alcohol, the presence of fermentable carbohydrates was detected by fermenting with yeast, when carbon dioxide was evolved, and the residue gave the iodoform reaction.

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[1] Zts. Schiess. Spreng. 1906, **1**, 405; 1907, **2**, 6184; J. S. C. I. 1906, **25**, 961; 1907, **26**, 35; abst. C. A. 1907, **1**, 358; Proc. Chem. Soc. **22**, 270; J. C. S. 1906, **89**, 1182, 1759; J. S. C. I. 1906, **25**, 868; Mon. Sci. 1908, **68**, 36; Chem. Centr. 1906, **77**, II, 1046, 1723; 1907, **78**, I, 538; Meyer Jahr. Chem. 1906, **16**, 325; 1907, **17**, 313.

They have also shown that the gradual decomposition of nitrocellulose which takes place on storage, is largely hydrolytic in nature, being brought about by the moisture of the air, under the influence of traces of acid liberated from the nitric esters[1]. When nitrocellulose is hydrolyzed in alkaline solution, nitrites are formed in considerable quantity, and various organic salts pass into solution, and that much more alkali is neutralized by nitrocellulose than can be accounted for by the nitroxyl groups present. They cite an instance where the ester contained 5.04 nitroxyl groups, but neutralized 9.2-9.5 equivalents of baryta, where if the nitroxyl groups only had entered into the reaction, but 5.04 equivalents of baryta would have been required.

Since nitrocellulose is gradually hydrolyzed both by hydrogen- and hydroxyl-ions, it follows that a slight hydrolysis must inevitably occur, even in pure water, owing to the minute dissociation of the water. Therefore on passing from alkaline to acid solution, the velocity of hydrolysis decreases to a minimum and then gradually increases again. Thus, although it is frequently assumed that absolutely pure water is without action on nitrocellulose, the assumption is correct only with certain reservations. Hydroxyl-ions are much more reactive than hydrogen ions, and hence the minimum velocity occurs in presence of a slight excess of hydrogen ions. The concentrations of hydrogen- and hydroxyl-ions necessary to produce the minimum velocity of hydrolysis can be calculated from the velocities of saponification in acid and alkaline solution respectively.

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[1] In this connection see E. Ador and A. Sauer, Zts. anal. Chem. 1878, **17**, 153. M. Hay, Mon. Sci. 1885, **27**, 424; Trans. Roy. Soc. Edin. 1885, **32**, 67. L. Maquenne, Ann. Chim. Phys. 1891, (6), **24**, 522. M. Berthelot, Ann. Chim. Phys. 1860, (3), **58**, 447; Compt. rend. 1900, **131**, 519. J. Nef, Ann. 1899, **309**, 181. L. Vignon and I. Bay, Compt. rend. 1902, **135**, 507; Bull. Soc. Chim. 1903, **29**, 507.

It has been found that at 37.8° the hydrolysis takes place with minimum velocity, when the concentration of the hydrogen ions is 3.7×10^{-6} and that of the hydroxyl ions 7.8×10^{-9}. Under these conditions the guncotton will liberate 5.6×10^{-5} gram-equivalents of acid per liter of water per year. In practice the decomposition is accelerated by the acid set free. Although gelatinized nitrocellulose differs so strongly from guncotton in the compactness, yet it undergoes a similar hydrolysis in the presence of alkalis. The saponification equivalent of a nitrocellulose of formula considered as containing 5.04 nitroxyl groups (containing 12.84% N) was found to be 85% in excess of the calculated.

The appearance of dry nitrocellulose and especially the gelatinized ester depends in a large measure upon the atmospheric conditions during storage. In a warm, dry atmosphere, sticks of gelatinized nitrocellulose gradually became brittle and the outer layer pitted, while the sticks shrank in size. At the same time, where deterioration is very marked, the color becomes darker. In a moist atmosphere there is formed sticky, deliquescent products, while the inner portion of the grains is found to consist chiefly of oxalic acid. During this deterioration the guncotton gradually loses its explosive properties, and in extreme cases can be burned only with difficulty. It has been shown that the rate of decomposition is much greater in a moist than in a dry atmosphere, due no doubt to the more favorable conditions for hydrolysis by acid decomposition products.

By storing at different temperatures, the decomposition is shown to be progressively more rapid as the temperature rises. Silberrad and Farmer state that at elevated temperature the velocity of decomposition is doubled by a rise of five degrees. This is an important point in the question of storage in hot climates, and indicates the need for frequent inquiry as to the stability of nitrocellulose when in storage.

Deterioration due to storage is shown by a loss both in weight and in nitrogen. In the former, a gradual but continual loss in weight during storage is noted, which has generally been assumed in the case of gelatinized nitrocellulose to be due to gradual volatilization of the gelatinizing constituents. However, the percentage of volatile matter does not materially decrease, the loss in weight being partially due to decomposition of the nitric esters, a fact confirmed by measurements of the velocity of gas evolution. A decrease in nitrogen percentage also takes place in long storage, indicating the breaking down of the nitric groups with formation of nitrogen oxides, which partially escape, and also catalytically act upon the remaining nitrocellulose.

The percentage of matter soluble in ether-alcohol also tends to increase, and the insoluble nitrocellulose to decrease. The acetone-insoluble residue shows a slight tendency to increase, probably due to the formation of insoluble decomposition products.

The fact noted[1] that cellulose nitrates sometimes contract mold, and the judgment of Sy[2] that denitrifying bacteria might start a decomposition, led B. Maļenkovic[3] to study the problem experimentally, from which he concluded that neither cellulose nitrates nor glycerol nitrates are directly decomposed by mold, but that the cellulose nitrates when placed in contact with organic matter are superficially decomposed. It appears, therefore, that danger of instability from mold is, at least, a remote one. It is to be noted that to prevent molding, small amounts of mercuric chloride are added to the cotton. Mercury possesses the property of combining with cellulose in a manner which causes the mercury to remain, even after repeated washings. Such nitrocotton containing mercury gives a factitious higher stability test.

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[1] The work of L. Vignon (Compt. rend. 1898, **126**, 1658; **127**, 872; abst. J. S. C. I. 1898, **17**, 794; 1899, **18**, 81; Chem. Centr. 1898, **69**, II, 422, 1246; Jahr. Chem. 1898, **51**, 1378) on the formation of oxy- and hydrocellulose shows plainly that cotton and cotton waste may, by the nature of the treatment to which they are subjected, be partly transformed into oxycellulose, which gives an unstable nitrate, and into hydrocellulose, which has a different rate of nitration than ordinary cellulose. A. Luck and C. Cross (J. S. C. I. 1900, **19**, 642; E. P. 5286, 1898) remove such foreign substances by means of acetone so diluted with water that it does not dissolve the higher nitrates. W. Will and F. Lenz (Ber. 1898, **31**, 68) have examined many nitrated carbohydrates for stability, in general finding them unstable.

O. Guttman, "Manufacture of Explosives," 1905, **2**, 49; cf. J. S. C. I. 1897, **16**, 283; 1898, **17**, 1180; 1899, **18**, 174, 857; 1901, **20**, 8, 609; 1902, **21**, 819, 1470; 1903, **22**, 511, 924, 1208; 1904, **23**, 953, 1903; 1905, **24**, 148, 347.

[2] Jour. U. S. Artil., Sept.–Oct., 1903; T. Bokorny (Chem. Ztg. 1896, **20**, 985; abst. J. C. S. 1898, **64**, ii, 39; Chem. Centr. 1897, **68**, I, 30; Jahr. Chem. 1896, **49**, 1031) found that cellulose trinitrate will serve as a food supply for molds, if suspended in distilled water containing the requisite amount of mineral matter, and placed in the dark. However, no growth was observed if mineral matter be absent.

[3] Rev. d'Art. 1908, **71**, 261; Mitteil u. Gegenstände J. Artill. u. Geniew. 1907, 509; abst. J. S. C. I. 1907, **26**, 1295. M. Jacque, Z. ges. Schiess. Spreng. 1910, **5**, 81, reports instances of blocks of compressed guncotton (containing 15% of water) showing very marked growths of microorganisms, but in no case was the nitrogen content or stability of the nitrocellulose affected. Attempts to cultivate the spores of *Aspergillus niger* and

A. Saposchnikoff,[1] in experimenting on cellulose nitrate of the formula $C_{24}H_{31}(NO_3)_9O_{11}$, found that the temperatures of de-

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Mycetozoa in nitroglycerol and ethyl and amyl nitrates were not successful. It is pointed out that the *algae* and aquatic plants produce organic salts, especially oxalates, during decomposition, and that traces of these organic salts would adversely affect the heat test of guncotton and nitroglycerol. In support of this view the author mentions that in 1907 one of the large dynamite factories in Mexico experienced great difficulty in obtaining heat tests up to their standard of fifteen minutes at 76°. Investigation showed that the cause of the trouble lay in the fact that the water reservoirs and channels had considerable quantities of vegetable growths in them, and when this was cleared away the heat tests of the guncotton and nitroglycerol returned to their normal figures.

Ulmic bodies, which are closely related to the higher members of the acetic series, may also influence the stability of a not thoroughly purified cellulose nitrate. A. Girard states (Ann. Chim. Phys. 1881, **24**, 337) that when hydrocellulose is heated above 80° it is converted into ulmic bodies possessing an acid reaction. A. Stern (J. C. S. 1904, **85**, 336) doubts the accuracy of this statement, but says that when care is taken to remove all traces of acids no such bodies are formed, but easily form with traces of acid.

According to F. Du Pont and F Sparre (U. S. P. 836704, 1906; abst. J. S. C. I. 1907, **26**, 553) a cellulose nitrate may be stabilized by removing by means of solvents a portion of the unstable bodies. Their process consists in agitating with nitrocellulose, suspended in a liquid in which it is insoluble, an emulsion of a solvent of nitrocellulose diluted by a substance which is insoluble in the liquid in which the nitrocellulose is suspended, and which is not a solvent of nitrocellulose, but is soluble in the nitrocellulose solvent. As an example: 1 part of nitrocellulose suspended in 8 parts of water is agitated with 1 part of amyl acetate diluted by 0.25 part of a liquid such as amyl alcohol or benzine. See U. S. P. 503583, 1893; E. P. 15865, 1893, for similar stabilizing processes.

[1] J. Russ. Phys. Chem. Soc. 1904, **36**, 669; abst. Chem. Centr. 1904, **75**, II, 685; J. S. C. I. 1904, **23**, 935. See J. Russ. Phys. Chem. Soc. 1900, **32**, 375; 1903, **35**, 506; Chem. Centr. 1900, **71**, II, 708; 1901, **72**, II, 1330; J. C. S. 1904, **86**, ii, 614; Bull. Soc. Chim. 1905, **34**, 1068; Rep. Chim. 1905, **5**, 186; Chem. Ztg. 1904, **28**, 574. J. Russ. Phys. Chem. Soc. 1906, **38**, 1192; abst. C. A. 1907, **1**, 1324; J. C. S. 1907, **92**, i, 390; Chem. Zentr. 1907, **78**, I, 1185; Jahr. Chem. 1905–1908, II, 977; Seventh Cong. Appl. Chem. 1909, III; C. A. 1909, **3**, 2223; J. S. C. I. 1909, **28**, 747; Meyer Jahr. Chem. 1909, **19**, 333; Wag. Jahr. 1909, **55**, I, 434; Zts. Schiess. Spreng. 1909, **4**, 441, 462; J. Russ. Phys. Chem. Soc. 1914, **46**, 1102; abst. C. A. 1915, **9**, 1900; J. S. C. I. 1915, **34**, 789.

composition can be divided into three zones. Between 160° and 150° all the nitrogen and most of the hydrogen is lost; between 145° and 130° less of both these elements are lost; at 125° and below, very little nitrogen is liberated, but the water formed is still high. Above 160° the substance explodes after thirty to forty minutes' heating. The substances liberated are carbon dioxide, nitric oxide, carbon monoxide, nitrogen, and water. The appearance of the residue varies considerably with the temperature to which the cellulose nitrate has been subjected. A curve is drawn showing the rate of decomposition at various temperatures, from which it is deduced that the rate of decomposition decreases with the fall in temperature. For the intervals 125°-140° $(dv/dt)_{max} = -24.6 + 0.201t$, and for 145°-155°, $(dv/dt)_{max} = -136.5 + 0.985t$.

In conjunction with W. Jagellowitsch,[1] he examined the rate of decomposition of a specimen of ordinary pyroxylin of the approximate composition $C_{24}H_{29}(NO_2)_{11}O_9$, at seven different temperatures between 120° and 150°. The method adopted consisted in measuring the volume of gas evolved from a weighed quantity of the pyroxylin in a definite interval of time at a given temperature[2] as recorded by A. Mittasch. Curves constructed by using the volume of gas (v) and the time (t) as ordinates had distinct bends, indicating the autocatalytic character of the reactions. The relation between the temperature and the maximum reaction-velocities $\left(\frac{dv}{dt}\right)$ corresponding to the bends in the curves, may be represented by two lines, corresponding to the equations:

$$\text{Between } 120° \text{ and } 130° \text{ C., } \left(\frac{dv}{dt}\right)_{max} = -2.22 + 0.0192t,$$

$$\text{Between } 135° \text{ and } 150° \text{ C., } \left(\frac{dv}{dt}\right)_{max} = -64.22 + 0.48t;$$

these lines intersect at the point corresponding to 135°. The gaseous decomposition products consisted of carbon dioxide, carbon monoxide, nitric oxide and nitrogen; the relative proportions of the different gases were not affected to any considerable extent by the temperature. At temperatures below 135° the solid residue contained no hydrogen, while at temperatures above 135° it contained hardly any nitrogen.

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[1] J. Russ. Phys. Chem. Soc. 1905, **37**, 822; abst. Chem. Centr. 1906, **77**, I, 339; J. S. C. I. 1906, **25**, 198; Meyer Jahr. Chem. 1905, **15**, I, 339; J. C. S. 1906, **90**, i, 68.

[2] Zts. ang Chem. 1903, **16**, 929; abst. J. S. C. I. 1903, **22**, 1203

A. Saposchnikoff and M. Borisoff[1] have determined that nitrocellulose decomposes, not only on ignition, but also at temperatures not sufficiently high to ignite it. On heating a mixture of nitrocellulose containing 13.25% of nitrogen with quartz sand in an electric thermostat at 150° ± 1°, it loses 41.3% of its weight and decomposes according to the equation: $C_{24}H_{29\cdot31}(NO_3)_{10\cdot7}O_{9\cdot31} = C_{20\cdot14}H_{8\cdot27}O_{22\cdot55}N_4 + 2.58NO + 1.88CO_2 + 1.981CO + 2.06N_2 + 10.52H_2O$. With nitrocellulose containing 12% of nitrogen, the loss in weight is 43.2% and the equation expressing the decomposition: $C_{24}H_{30\cdot72}(NO_3)_{9\cdot28}O_{10\cdot72} = C_{20\cdot82}H_{4\cdot8}O_{19\cdot5}N_{2\cdot76} + 1.52NO + 1.42CO_2 + 1.764CO + 2.50N_2 + 12.96H_2O$.

On comparing these results with the following equations, representing the changes on igniting the nitrocellulose: (1) $C_{24}H_{29}(NO_3)_{11}O_9 = 12CO_2 + 12CO + 8.5H_2 + 5.5N_2 + 6H_2O$ and (2)$C_{24}H_{31}(NO_3)_9O_{11} = 6.84CO_2 + 16\ 51CO + 0.643CH_4 + 7.39H_2 + 4.5N_2 + 4.92H_2O$, it will be seen that the slow combustion occurring at the lower temperatures differs from the ignition in yielding a solid nitrogenous residue, in giving nitric oxide (and, at the beginning of the reaction, nitrogen peroxide), and in yielding no hydrogen but an increased proportion of water. When heated at 150° without sand, the nitrocelluloses decompose more rapidly and completely. Thus, the one containing 13.25% of nitrogen loses 91.1% of its weight; 63.2% of this loss is water and the rest a gaseous mixture having the percentage composition· NO, 27.74; CO_2, 25.10; CO, 17.44; N_2, 29.72.

At 135° gaseous mixtures were obtained from the two nitrocelluloses having the percentage compositions by volume:

	Nitrocellulose with 13.25% N	Nitrocellulose with 12% N
NO.	34.52	28.33
CO_2.	29 38	21.33
CO.	13.43	19.67
N_2.	22.67	30.67

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[1] J. Russ. Phys. Chem. Soc. 1904, **36**, 836; abst. J. C. S. 1904, **86**, i, 799; Jahr. Chem. 1904, **57**, 1167; Chem. Centr. 1904, **75**, II, 1030; Meyer Jahr. Chem. 1904, **14**, 369; J. S. C. I. 1904, **23**, 1112.

In determining the stability of nitrocellulose and smokeless powders derived therefrom towards ultra-violet light, D. Berthelot and H. Gaudechon[1] placed samples over mercury in an atmosphere of CO_2 and N enclosed in quartz tubes and exposed to the rays from a quartz lamp at controlled temperatures much below those at which other portions of the same samples evolved gas. All samples gave CO, CO_2 and N, and all but the French Service powder "B" gave N_2O_2, the powders such as cordite M.D. which contain nitroglycerol, yielding the most.

They also exposed nitrocellulose and nitroglycerol powders for 6 hours in thin quartz tubes to the rays from a mercury vapor lamp, the tubes being filled either with neutral, oxidizing or reducing gases, temperatures being 25°–28°, 40° and 70°–75°, and the samples placed 70–80, 50, and 15 mm. respectively from the lamp. It was shown by parallel experiments that no gases were liberated from the effect of the temperature alone, but did take place from the ultra-violet light, and in the same manner as the slow decomposition normally occurring from the effects of heat, moisture, etc. The absence of methane and hydrogen, which are characteristic gases of explosion, was noted.

Nitrocellulose[2] (collodion cotton) when exposed to the mercury vapor lamp, was found to evolve a mixture of CO_2, CO, N_2, N_2O and NO, containing as much as 40% NO, but showed a lower stability than "B" powder. In tests of two 6-year old service powders, one stabilized with diphenylamine, the other with amyl alcohol, the former yielded gas containing 14%, the latter 1.7% NO at 75° and 20 mm. from the source of light, while both gave no NO at a greater distance and lower temperature. In the first instance decomposition was too rapid to be prevented by the presence of the stabilizers.

E. Berger[3] has contributed to the discussion of the theory of decomposition of the cellulose nitrates, he holding that the first reaction is a saponification of the nitrocellulose molecule, the HNO_3 formed being immediately reduced to NO_2. This is absorbed still further and reduced by more ester. The first period of alteration is unaccompanied by any observable phenomenon, but after a time the material loses its power of reducing the NO_2 and the HNO_3 and HNO_2 formed, in the presence of water, begin to accumulate in the cellulose ester. During this first period while the guncotton is capable of reducing the NO_2 formed, there is a sort of reserve of stability and the powder is not dangerous. Therefore the problem of stabilization is to prolong this first period as much as possible by adding something to absorb or neutralize the NO_2 formed. The hypothesis is certainly ingenious, and there are facts known which appear to accord with the ideas advanced.

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[1] Compt. rend. 1911, **153**, 1220; abst. C. A. 1912, **6**, 806; J. C. S. 1912, **102**, ii, 210; J. S. C. I. 1912, **31**, 47; Chem. Zentr. 1912, **83**, I, 534. See also Zts. Schiess. Spreng. 1912, **7**, 52; abst. C. A. 1912, **6**, 1225; Meyer Jahr. Chem. 1911, **21**, 341, 344.

[2] D. Berthelot and H. Gaudechon, Compt. rend. 1912, **154**, 201, 514; abst. C. A. 1912, **6**, 2530; J. S. C. I. 1912, **31**, 204, 303; J. C. S. 1912, **102**, i, 163; ii, 394; Chem. Zentr. 1912, **83**, I, 684, 1266.

[3] Bull. Soc. Chim. 1912, **11**, I–XXV; abst. C. A. 1912, **6**, 3518; Chem. Zentr. 1912, **83**, II, 463.

The unstable cellulose nitrates removed by the dehydration process with 94%-95% alcohol has been reported upon by F. Langenscheidt,[1] he having found the alcohol after use to contain 5-7 gm. per liter of soluble products of about 9.5% N, evolving 3.2 cc. NO per gm. in the Obermüller test at 135°. The material was obtained by evaporation of a portion of the alcohol and precipitation with water, followed by long drying at low temperature. The precipitate obtained is colloidal, not readily filtered, and it was observed that the stability of the cellulose nitrate from which this material was removed was appreciably increased by the alcohol solvent treatment.

According to E. Trapani,[2] if a small quantity of straight cellulose nitrate or smokeless powder such as ballistite or cordite, be carefully heated until it deflagrates, a pungent odor resembling that of formaldehyde is observable. Further, if the cold residue is treated with water and sodium carbonate to neutralize the nitrous acid formed, the liquid obtained, gives with phenylhydrazine hydrochloride and sodium nitroprusside, the blue coloration characteristic of the presence of formaldehyde. The author considers that the formaldehyde may be derived from the residue $CH(OH).CH_2OH$, possibly existing in the cellulose nitrate or from some analogous chain formed in the early stage of the decomposition as the result of processes of denitration. Hydroxypyruvic acid constitutes one of the thermal decomposition products of cellulose nitrate, and this may yield formaldehyde by further degradation. Its presence is also probably related to that of carbon monoxide and hydrogen, which are formed on explosion of this ester.

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[1] Zts. Schiess. Spreng. 1914, **9**, 54; abst. C. A. 1914, **8**, 1669. Bravetta and Parozzani, Zts. Schiess. Spreng. 1908, **3**, 233; abst. Wag. Jahr. 1908, **54**, I, 450.

[2] Atti. R. Accad. Lincei, 1917, (5), **26**, i, 332; Gazz. chim. ital. 1917, **47**, I, 250; abst. Chem. Zentr. 1917, **88**, I, 255; Meyer Jahr. Chem. 1917, **27**, 163; C. A. 1918, **12**, 368, 1291; J. S. C. I. 1917, **36**, 907; J. C. S. 1917, **112**, i, 380.

Reference has previously been made (see p. 1719) to the action of calcium carbonate upon nitrocellulose, and the practice of adding small amounts to guncotton as a preservative and antacid. An important contribution to this subject has recently appeared by T. Lowry, K. Browning and J. Farmery.[1]

As far back as 1847, P. v. Kerckhoff and F. Reuter[2] studied the decomposition of pyroxylin by steam at 100°, and obtained "cellulose dinitrate" or *typhoxylin*, as the principal product, containing 6.66% N, and record the separation of a lead salt which undoubtedly is identical with the lead hydroxypyruvate prepared by W. Will in 1891.[3]

In 1885 M. Hay[4] recorded the production of potassium acetate and formate, together with potassium nitrite and nitrate in the ratio $KNO_3.2KNO_2$. M. Berthelot[5] described the formation of polymerization products of aldehyde by the action of KOH on ethyl nitrate, and suggested that the formation of nitrites in the action of KOH on nitroglycerol might be due to a decomposition of the nitric ester into glyceraldehyde. Silberrad and Farmer (see p. 1707) also detected acetic, formic, nitric and nitrous acids

[1] J. C. S. 1920, **117**, 552. See also P. Vieille, Mem poudres, **15**, 61, 71, 89; abst. Arms Expl. 1910, **5**, 64; C. A. 1910, **4**, 961, 1101, 1371. L. Leheure, Mem. poudres, **15**, 1; abst. C. A. 1910, **4**, 1371, 2204.

[2] J. prakt. Chem. 1847, **40**, 262, 284; Compt. rend. 1847, **24**, 46; abst Liebig & Kopp's Ann. Rept. 1847–1848, II, 363; Jahr. Chem. 1847–1848, **1**, 1129. Compare also the résumé of the investigations upon guncotton, J. prakt. Chem. 1847, **40**, 193; 1848, **43**, 242; Ann. 1848, **65**, 391; Chem. Centr. 1847, **18**, 690.

[3] Ber. 1891, **24**, 400; abst. J. S. C. I. 1891, **10**, 578; J. C. S. 1891, **60**, 542; Chem. Centr. 1891, **62**, I, 530; Jahr. Chem. 1891, **44**, 1624; Chem. Ztg. Rep. 1891, **15**, 90; Bull. Soc. Chim. 1891, **6**, 668; Meyer Jahr. Chem. 1891, **1**, 333.

[4] Trans. Roy. Soc. Edin. 1885, **32**, 67; abst. J. C. S. 1885, **48**, 742; Proc. U. S. Nav. Inst. 1886, **12**, 182; Ber. 1886, **19**, 268; Wag. Jahr. 1886, **32**, 319; Chem. Tech. Rep. 1886, **25**, II, 295; Mon. Sci. 1885, **27**, 424; J. S. C. I. 1885, **4**, 417.

[5] Compt. rend. 1900, **131**, 519; abst. J. S. C. I. 1900, **19**, 1038; Tech. Chem. Jahr. 1900, **23**, 151; Jahr. Chem. 1900, **53**, 614; Chem. Centr. 1900, **71**, 891; J. C. S. 1900, **78**, i, 620.

among the products of decomposition of nitrocellulose which had been stored at 54° for 23 weeks, but did not find glycerol or cellulose among the products of decomposition of cordite by water or in the presence of alkalis.

E. Berl and M. Delpy[1] (see p. 1663), acting on nitroglycerol by alcoholic KOH, isolated glyceryl *aa'*-dinitrate, but were unable to detect either the mono-nitrate or glycerol itself.

T. Lowry and co-workers, as the result of their investigations upon the decomposition of nitric esters, especially nitrocellulose and cordite by lime, have deduced the following:

1. Hydrolysis or saponification of the normal type is not the predominant action when cordite is decomposed by lime in the presence of pyridine.

2. Traces of glycerol were detected only when a very large excess of pyridine was used; these conditions were also the only ones in which a clean, crystalline calcium nitrate was obtained. The calcium dihydroxypyruvate is, however, an important product of the reaction.

3. Two partly denitrated celluloses, corresponding approximately with the formulas $C_{12}H_{18}O_8(NO_3)_2$ and $C_{12}H_{17}O_7(NO_3)_3$, were obtained as by-products of incomplete decomposition, but no cellulose was obtained when the decomposition was carried to completion.

4. The main action, therefore, appears to be a decomposition of the nitric ester into a ketone or aldehyde and a nitrite, instead of a hydrolysis to an alcohol and nitric acid.

The broad question of stabilization of cellulose esters is in such a state of fluxation—a transition stage in which generalizations should be drawn with extreme caution—that in the following general summary of our present knowledge of this subject, only the points are emphasized which appear to be fairly well established, or upon which there is but little controversy.

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[1] Ber 1910, **43**, 1421. In this connection see A. Williamson, Proc. Roy. Soc. 1854, **7**, 130. R. Railton, J. C. S. 1855, **7**, 222. P. Hess, Zts. anal. Chem. 1874, **13**, 257. A. Sauer and E. Ador, Ber. 1877, **10**, 1982. F. Hess and J. Schwab, Sitz. Ber. Wien. Akad. 1877, (2), **75**, 702; Ber. 1878, **11**, 192. W. de la Rue and H. Mueller, Ann. 1859, **109**, 122. C. Beckerhinn, Jahr. Chem. 1876, **29**, 1009. T. Carlson, Ber. 1907, **40**, 4191. W. Will, Ber. 1908, **41**, 1114. J. Brühl, Ber. 1878, **11**, 192. A. Baeyer and V. Villiger, Ber. 1901, **34**, 755. H. Debus and N. Socoloff, Ann. 1858, **106**, 79, 95. E. Berl, Chem. Ztg. 1910, **34**, 429. E. Berl and A. Jurrissen, Zts. ang. Chem. 1910, **23**, 241. E. Berl and W. Smith, Ber. 1907, **40**, 905. J. Meidenheimer and F. Heim, Ber. 1905, **38**, 3834. Petriew, J. Russ. Phys. Chem. Soc. 1879, **10**, 72.

1. Nitrated cellulose upon removal from the nitrating vessel contains considerable amounts of free and some combined nitric and sulfuric acids, which if not removed would soon render the product sufficiently unstable to be worthless.

2. These products consist of lower cellulose nitrates of a type of deficient stability, together with (probably) nitrated degradation products of cellulose such as the nitrates of oxycellulose and hydrocellulose, removable by alcoholic dehydration.

3. Organic sulfuric esters are formed in relatively small amounts, which upon storing split off sulfuric acid, thereby lowering stability, but which are removable by a series of preliminary boils in a slightly acid medium, i. e., in presence of the acid remaining mechanically attached to the nitrated product, it having been shown that the sulfuric esters are more readily decomposed by acid solutions than by alkaline liquids, the latter appearing to fix the sulfuric group.[1]

4. In the case of the lower types of cellulose nitrates, they are more readily attacked by alkalis, and therefore the acid boils should be succeeded by a series of short alkali boils to complete the stabilization, but not continued too long.[2]

5. The nitric acid used for esterifying should be as free as

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[1] R. Robertson (J. S. C. I. 1906, **25**, 264) has shown that the sulfuric acid esters are more readily decomposed by acid solutions than by alkalis. This is similar to the behavior of the cellulose aceto-sulfates (see Vol. VIII of this series) as described by Cross and Bevan (Ber. 1905, **38**, 1859). Even with cold water the sulfuric acid residue was split off, but much more rapidly with boiling water, whereas alkaline solutions eliminated the whole of the acetic acid residue by saponification, leaving the sulfuric acid ester intact. This is further explained by J. Briggs (J. S. C. I. 1906, **25**, 626) who points out that the sulfuric acid residue in the form —SO_4H is readily hydrolyzed by water or acids, but becomes —SO_4N with alkalis, to which it is remarkably stable. Robertson's experiments above, elsewhere referred to, therefore pointed to the desirability of the initial boilings being long to allow acidity to develop. For this reason the guncotton should not be freed entirely from the acids of nitration, an acidity of about 1% calculated on the weight of the nitrocellulose having been found beneficial.

[2] In the case of the nitric esters, these are readily attacked by alkalis, and appear to be best removed by a series of short alkaline boils, which should not be continued too long, or decomposition of the cellulose nitrate will result by hydrolysis, and the solubility be diminished and the clarity of the solutions decreased. Silberrad and Farmer (J. C. S. 1906, **89**, 1759) measured the velocity with which nitrocotton is hydrolyzed by a solution of barium hydroxide, and show that it is about 480 times that of the acid hydrolysis for the same strength of solutions. It therefore is inadvizable to use strong alkaline solutions. Alkaline hydroxides should be avoided and sodium carbonate used only when the water contains no natural alkalinity.

possible from nitrous acid, on account of the possibility of the formation of cellulose nitrites (which see) of deficient stability.[1]

6. The sulfuric acid content of the nitrating bath should be kept as low as possible.[2]

7. When nitrocellulose is prepared by the displacement method, stabilization is apparently best obtained by a number of long boilings, followed by a series of shorter ones.[3]

8. The initial cellulose esterified should be as free from extraneous matter as is possible without submission to a drastic purification.[4]

9. Stability is a *relative* not an *absolute* expression, efforts being to *minimize* and not to *prevent* decomposition.

10. The nearer the approach of the preparation of an ester of definite composition, rather than a series of esters of gradually rising nitrogen content, the more nearly permanent can the product be stabilized by proper treatment.

11. The *keeping qualities* of properly nitrated cellulose are functions of the temperature to which it is subjected upon storage

[1] P. Nicolardot and G. Chertier (Compt. rend. 1910, **151**, 719) have prepared cellulose nitrites (which see), which are very unstable, the higher nitrites decomposing before they can be analyzed. A. Schrimpf (Zts. Schiess. Spreng. 1919, **14**, 41) shows that nitration of cellulose with mixed acids containing nitrous acid gives nitrous esters which are more unstable than the normal ester. His view, however, is that instability is not so much due to sulfuric esters as to the corresponding esters of oxycellulose.

[2] A. Herve (Mon. Sci. 1918, **85**, 193, 241) finds that the proportion of sulfuric ester increases as the nitric acid content of the nitrating mixture is lowered and the sulfuric acid raised. As the percentage of sulfuric acid increases, the stability is lowered.

[3] The first few boilings are carried out in acid water, being so regulated that the acidity in the fiber is sufficient to neutralize the alkalinity present in the water.

[4] Will and Lenz (Ber. 1898, **31**, 68) consider some of the instability in nitrocellulose comes from the presence of impurities present in the original cotton, and not completely removed. No doubt in the boiling process, the major portion of these impurities are hydrolyzed. W. Will (Gummi. Ztg. Celluloid Suppl. 1906, **5**, 21) considers that the addition of alkali is worthless, and O. Guttmann (Zts. ang. Chem. 1898, **11**, 1103) considers that the practice of adding calcium carbonate to wet guncotton should be discontinued.

In the selection of a suitable substance for checking or diminishing the decomposition of nitrocellulose, it is advizable to employ a product which is soluble in the gelatinizing agent, otherwise the stabilizer is apt to become mixed irregularly. It is also necessary that it should be sufficiently nonvolatile, so as not to appreciably evaporate during storage of the nitrocotton, and should be substantially non-deliquescent. The compounds employed for this purpose (see Vol. II) should be basic in nature, or if non-basic should be capable of reacting with nitrous and nitric acids, the bulk of the substances employed for this purpose containing either an ethenoid linking or carbonyl groups.

after once having been properly purified. Attempts to calculate a *modulus of decomposition*, as a measure or parameter of function or effect, leave many points as yet unexplained.

12. There are two points in connection with deterioration of cellulose esters to bear in mind, one being the time before deterioration commences, and the other the speed of decomposition, once it has commenced. There is no observable or analytically distinguishable line of demarcation between the two, although the question is of exceeding importance and has been discussed at great lengths.

13. Deterioration may be *inhibited*, but cannot be *prevented*. Once *initiated*, it may be *attenuated*, but not entirely *overcome*.

14. The importance of stability is directly as the length of time the material is stored before use, i. e., in the peaceful arts it has been given less thought than with nitrocellulose for explosives, because in the former the material is used shortly after manufacture. However, this is an erroneous attitude to take.[1]

15. Deterioration in general depends upon (a) initial purity; (b) height and uniformity of temperature during storage; (c) atmospheric humidity; and (d) free access to pure air, frequently changed.

Nitrocellulose Solubility. The various nitrocelluloses are soluble, or nearly so, in anhydrous acetone, and to a less degree in ethyl and amyl acetates and other esters. In the aliphatic acetic esters, with increase in molecular weight of alkyl, comes decreased solubility, i. e., methyl acetate is a more complete (not better) solvent for the nitrocelluloses than is amyl acetate. But inasmuch as the hygroscopicity of these esters decreases with increasing molecular weight, the higher esters (butyl and amyl acetate) are preferable as solvents in commercial pyroxylin mixtures.

They are generally insoluble in water, benzine, benzene, chloroform, carbon tetrachloride, or fixed oils. All except the lower members (the commercially worthless nitrocelluloses) are insoluble in pure ethyl ether or alcohol separately. The commercial nitrocelluloses contain small amounts of fatty matter and resins, obtained in most cases from the original cellulose, and these bodies are removable by Soxhlet extraction by ether, although in properly purified cotton, the amount of such extractive will usually be found under 1%. Ethyl alcohol is a solvent only when absolute or nearly so, while methyl alcohol is a much more energetic solvent.

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[1] It is lamentable that the importance of thorough stabilization is insufficiently appreciated by users of nitrocellulose in the peaceful arts, for a proper realization of the fact that inferior technical results are often due to incomplete stabilization undoubtedly accounts for much of the inferior solutions, plastics and artificial leather coatings which have been placed upon the market. In the manufacture of nitrocellulose for propellants, the question of stability is one of self-preservation, because the material is generally stored for a considerable length of time before use. The common effects of incomplete stabilization in the non-explosive arts are brittle films, discoloration of dyestuffs when added to colored lacquers, and the peeling of coating when placed on textile or metal. In the celluloid industry, considerable improvements in ensuring stability have recently been made.

The nitrogen content is not a trustworthy criterion of solubility, for nitrocelluloses are known containing 10%-11% N which are, or are not soluble in amyl acetate. For example, a cotton may be nitrated at a comparatively low temperature, and after nitration is substantially complete so far as nitrogen content of the nitrocotton is concerned, if a sample be withdrawn, and washed to neutrality in the usual manner, while the bulk of the nitrated cotton remains in the nitrating mixture, the temperature of which is considerably elevated, it is possible to produce two nitrocottons, in which the sample first withdrawn is completely soluble in alcohol-ether mixture, while the latter sample is substantially insoluble therein, both containing approximately the same nitrogen content. The latter sample will have a lower viscosity. There apparently has, as yet, been elucidated no law between solubility, viscosity and nitrogen content of nitrocelluloses, and many apparently inexplicable anomalies exist in this field, quite familiar to those who have *lived* this art, as distinguished from those who have merely *studied* it.

The so-called "soluble" nitrocelluloses are distinguished from the highly nitrated guncottons by a solubility in ether-alcohol, i. e., ethyl ether and ethyl alcohol, but not in a mixture of any ether or any alcohol. The commercially valuable cellulose nitrates are mainly the eight and nine nitric group cellulose esters. Eder calls his pentanitrocellulose (C_{12}) soluble. Mendelejeff has described a soluble nitrocellulose (in alcohol-ether) with 12.4% N, while Vieille, as well as Lunge and Weintraub, were able to obtain a soluble ester with twelve nitric groups (decanitrocellulose). Therefore, it appears that two decanitrocelluloses exist, or that two combinations of lower and higher nitrated celluloses are possible of this nitrogen content, which are or are not soluble in ether-alcohol.

H. Roscoe has found a soluble as well as insoluble nitrocellulose (12.8% N) in connection with his cordite investigations. Lunge and Bebie obtained a completely soluble compound with 13.02% N (207.7 cc. NO), and Aspinwall reports he has succeeded in preparing a soluble nitrocellulose of 12.91% N, a statement corroborated by R. Schüpphaus. Lunge has advanced the opinion that methods which lead to the formation of soluble nitrocelluloses consist in the formation of simpler bodies which are soluble.

From determinations of the viscosity of mixtures of various alcohols and ethers, F. Baker[1] deduced that dissociation of the alcohols takes place in such mixtures, but this dissociation is probably associated with the formation of an ether-alcohol complex, and to this complex the solvent power of these mixtures for nitrocellulose is due. There is no definite distinction between viscosity-concentration curves (see next topic) showing maxima or minima, and those in which the viscosities all lie between those of the two components. He established that the relation derived by C. Lees[2] is purely empirical, and of strictly limited application. The evidence found by Baker of the formation of compound molecules such as C_2H_6O, $C_4H_{10}O$, which apparently have the property of dissolving the nitrocellulose, has been questioned by E. Bingham[3] as being inconclusive. He puts forward an alternative theory in which ether plays but a passive rôle in causing the associated alcohol molecules to split up into simple molecules, and these latter dissolve the cellulose nitrate. This theory, however, is not applicable to many solvent combinations.

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[1] J. C. S. 1912, **101**, 1409; abst. C. A. 1912, **6**, 3042; Bull. Soc. Chim. 1913, **14**, 3; Chem. Zentr. 1912, **83**, II, 527. See also M. Appleby, J. C. S. 1910, **97**, 2000. E. Berl and R. Klaye, Zts. Schiess. Spreng. 1907, **2**, 381. O. Faust, Zts. physik. Chem. 1912, **79**, 97. W. Ramsay and J. Shields, Zts. physik. Chem. 1893, **12**, 433. A. Dunstan, J. C. S. 1904, **85**, 817; 1907, **91**, 83; 1909, **95**, 1556.

[2] Phil. Mag. 1901, (6), **1**, 128; abst. J. C. S. 1901, **80**, ii, 148.

[3] J. C. S. 1913, **103**, 1266; abst. C. A. 1913, **7**, 3438; J. S. C. I. 1913, **32**, 511; Bull. Soc. Chim. 1913, **14**, 1122; Chem. Zentr. 1913, **84**, II, 924. See also R. Pribram and A. Handl, Wien. Akad. Ber. 1878, **78**, II, 113. T. Thorpe and J. Rodger, Phil. Trans. 1894, **185A**, 397, 403; G. Knibbs, J. Roy. Soc. New South Wales, 1894, **29**, 77; 1896, **30**, 186; cf. Zts. physik. Chem. 1912, **80**, 685. J. Traube, Ber. 1886, **19**, 871. E. Hagenbach, Pogg. Ann. 1860, **109**, 385. R. Gartenmeister, Zts. physik. Chem. 1891, **6**, 524. H. Jacobson, Arch. f. Anat. Physiol. 1860, 80. M. Couette, Ann. Chim. Phys. 1890, (6), **21**, 433. Wilberforce, Phil. Mag. 1891, **31**, 407. J. Boussinesq, Compt. rend. 1890, **110**, 1160, 1238; 1891, **113**, 9, 49. O. Reynolds, Phil. Trans. 1883, **174**, 935; 1886, **177A**, 157. E. Bingham and T. Durham, Amer. Chem. J. 1911, **46**, 281. A. Findlay, Zts. physik. Chem. 1909, **69**, 203. H. Jones and E. Bingham, Amer. Chem. J. 1905, **34**, 545; 1906, **35**, 195. See also J. A. C. S. 1911, **33**, 1257; Physical Review, 1912, **35**, 407. G. White, J. Ind. Eng. Chem. 1912, **4**, 267.

N. Stepanow[1] found that the maximum solubility is obtainable when the proportion of alcohol to ether is as 2 to 3, i. e., when the liquids are mixed in about stoicheiometrical proportions. The additions of such solvents as acetone, methyl acetate, ethyl acetate, amyl acetate increases the solvent power of ether-alcohol, while amyl alcohol, benzene, benzine, carbon tetrachloride and chloroform attenuate it. The general subject of cellulose ester solubility forms the subject matter of Volume II of this series, to which the reader is referred for details.

The "low nitrogen" nitrocelluloses are in general soluble in a wider range of solvents, than those of higher nitration, although this generalization must be accepted with reserve due to the influence which the temperature of nitration exerts on the solubility, with but a decreased change in nitrogen content. Thus a "11% N" material is usually completely soluble in ether-alcohol, while a "13% N" cellulose nitrate may show only a 1%-12% solubility. It should be emphasized that nitrogen content is but *one* of the factors governing solubility, and the heterogeneous solubility determinations to be found in the literature made by investigators of unimpeachable integrity, undoubtedly in many instances, may be traced to insufficient recognition of the necessity of using pure solvents, and of obtaining solubility determinations in a strictly comparable manner. In this connection it should be noted that commercial ether usually contains a small amount of alcohol, and if an ether of this kind be employed for solubility examinations, some of the nitrocellulose may be dissolved due to the presence of the alcohol in the ether used. The specific gravity of ether used for this purpose should not exceed 0.72.

Many of the nitrocelluloses may be roughly characterized by varying degrees of solubility in a mixture of alcohol and ether, but no clear-cut line of demarcation can be drawn by this test. Only as a generality may it be safely said that the ether-alcohol

[1] Zts. Schiess. Spreng. 1907, **2**, 43; abst. C. A. 1907, **1**, 1059; Chem. Zentr. 1907, **78**, I, 1109; Jahr. Chem. 1905-1908, II, 975.

solubility increases with a decrease in nitrogen in nitrocellulose.

The varying solubility of nitrocelluloses of different nitrogen content has been taken advantage of by C. Curtis and G. Andre,[1] who treat a guncotton containing certain mixtures of cellulose di- and trinitrates with a solvent capable of dissolving the former only. In this way the particles of the trinitrate (C_6 basis) become coated with, and cemented together by, the dissolved dinitrate. The pellets are hardened by removal of the solvent by any of the usual methods.

Somewhat similar is the blending method of the International Smokeless Powder & Chemical Co.,[2] who mix in an acetone solution, nitrocelluloses of 13.75% and 12.75% N respectively, so as to produce an explosive of a definite nitrogen content and propulsive power. By manipulating the proportion of the two nitrocottons introduced, corresponding variations in viscosity, toughness and hardness of the colloid are said to be produced.

The statement is found in the literature that all forms of cellulose nitrate are soluble in acetone and acetic ether, and a rough method of estimating unchanged cellulose has been suggested by dissolving the cellulose nitrate in one of these solvents, the insoluble portion being cellulose. In many examinations of ethyl acetate-insoluble residues from cotton nitration, the author has yet to find one free from nitrogen, even after the acetate has been left in contact with the nitrated cotton for periods of as long as two weeks, with daily change of solvent. The percentage of nitrogen as calculated on the sample dried at 100° has varied from 0.2–4.7, thus indicating the presence of nitrogen-containing bodies in nitrocotton, insoluble in ethyl acetate. The anomalous results in solubility reported by different investigators render accurate generalizations impossible at the present time. A nitrocotton of 12.5% nitrogen may be practically insoluble in ether-alcohol or may entirely dissolve to a clear and fluid solution.

Bruley[3] has studied in great detail the influence of various mixed acids and time of nitration on the solubility of the resulting nitrocellulose. The results of nitration he finds depend on the duration of steeping, the temperature of dipping and steeping, and the subsequent steps in purification. In order to produce the same degree of nitration, the steeping should be prolonged in proportion as the nitric acid is reduced in the mixed acids. The influence of time of nitration on the "NO_2" content and solubility is shown in the following table:

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[1] U. S. P. 575765, 1897. E. P. 19068, 1891; abst. Chem. Centr. 1893, **64**, I, 808; J. S. C. I. 1893, **12**, 63; Chem. Tech. Rep. 1893, **32**, I, 237; Tech. Chem. Jahr. 1892–3, **15**, 177. Nor. P. 3201, 1892. Can. P. 41524, 1893.

[2] E. P. 13457, 1903; abst. Chem. Ztg. 1904, **28**, 1030; J. S. C. I. 1903, **22**, 963.

[3] Mem. des Poudres, 1895–96, **8**, 111.

TABLE CXIX—SOLUBILITY OF NITROCELLULOSE

Duration of Steeping	Inferior Colloid		Superio Colloid		Guncotton	
	I		II		III	
	NO_2 Content, Cc.	Solubility %	NO_2 Cc.	Solubility %	NO_2 Cc.	Solubility %
1 hr.	165.8	91.7	186.8	94.9	206.4	10.9
2 hrs	166.8	95.5	189.0	95.0	209.4	8.3
4 hrs.	167.8	93.0	191.8	96.2	209.2	6.8
6 hrs.	167.8	94.8	198.0	94.1	210.2	6.7
8 hrs.	166.8	95.4	191.8	96.7	210.2	5.6
12 hrs.	..	.	.	.	210.8	7.4
24 hrs.	166.8	98.1	194.0	96.6	210.6	10.6

Increase of temperature up to 26° increases solubility with "colloids" and has a similar tendency with guncottons.

The following table shows the great variation in solubility with alteration in acid mixture and time of steeping. (Bruley's researches had in view the securing of a certain desired product in the nitration of cellulose.)

H. de Chardonnet[1] prepares a readily soluble nitrocellulose by heating the cellulose previous to nitration in a current of air at 150°-170° for 4-8 hours. E. Berl[2] heats the cellulose in an inert gas (oxygen-free), such as carbon dioxide, to a high temperature. O. Glum & Co.[3] heat it with glycerol or oil to 120°-140°. The

[1] E. P. 19560, 1891; abst. J. S. C. I. 1892, **11**, 939; J. Soc. Dyers Col. 1892, **8**, 19.

[2] Zts. Scheiss. Spreng. 1909, **4**, 81; abst. C. A. 1909, **3**, 1926; J. S. C. I. 1909, **28**, 380; Chem. Zentr. 1909, **80**, I, 1275; Jahr. Chem. 1909, **62**, II, 384; Meyer Jahr. Chem. 1909, **19**, 335; Wag. Jahr. 1909, **55**, I, 431.

[3] D. R. P. 217316, 1908; abst. Chem. Zentr. 1910, **81**, I, 490; Chem. Ztg. Rep. 1910, **34**, 47; Chem. Zts. 1909, **9**, No. 1670; Wag. Jahr. 1910, **56**, II, 433; Zts. ang. Chem. 1910, **23**, 526.

TABLE CXX.—SOLUBILITY OF NITROCELLULOSE

No. of Mixture	Composition			General Results as Affected by the Time of Steeping								
				6 Hours			12 Hours			24 Hours		
	H_2SO_4	HNO_3	H_2O	NO_2 Cc.	Solubility %	Viscosity Degree in Scale	NO_2 Cc.	Solubility %	Viscosity Degree in Scale	NO_2 Cc.	Solubility %	Viscosity Degree in Scale
I	The weight of H_2SO_4 used (1.5 kilos) taken as the base of comparison and constituted 100/100. 65.8° Baumé; about 5% of water.	55/100	28.8/100	196.2	99.0	195	197.2	97.0	206	...	..	...
II		45.9/100	24.3/100	205.0	52.9	...	205.8	52.9	...	...	..	...
III		37.2/100	18.3/100	206.8	2.6	...	209.6	2.4	...	...	..	...
IV		18.3/100	13.1/100	295.8	5.2	...	203 2	5.2	...	205.2	2.5	...
V		9.1/100	10.9/100	122.6	19.8	...	128.2	20.1	...	134.0	14.2	...
VI		9.4/100	21.3/100	143.0	19.1	...	142.8	19.4	...	147.8	21.9	...
VII		18.0/100	20.8/100	183.4	89.7	52	182.0	90.9	45	...	..	...
VIII		17.6/100	33.2/100	Cotton dissolved in acid			Cotton dissolved in acid			Cotton dissolved in acid		
IX		28.8/100	22.0/100	196.2	95.4	117	196.2	97.2	108	...	..	...
X		37.5/100	29.3/100	184.6	96.3	86	186.2	95.8	90	...	..	...
XI		54.9/100	37.8/100	164.4	87.5	56	164.6	94.4	41	172.6	95.3	45
XII		47.0/100	34.6/100	171.6	92.8	...	172.6	96.8	40	177.0	96.4	74
XIII		27.5/100	33.3/100	153.4	47.0	...	154.2	61.8	...	157.2	66.0	...
XIV		37.3/100	38.0/100	144.4	16.0	. .	146.2	14.0	...	146.8	10.8	...
XV		47.6/100	45.4/100	121.6	1.4	...	123.6	1.5	...	142.8	1.9	...
XVI		54.1/100	34.5/100	174.2	94.8	33	178.6	96.5	45	178.2	91.6	151
XVII		45.1/100	28.3/100	185.0	96.9	40	186.2	97.8	51	...	..	...
XVIII		45.4/100	38.4/100	155.2	26.0	...	155.6	39.8	...	152.8	21.8	...
XIX		36.5/100	23.7/100	197.6	92 2	178	199.8	91.3	122	...	..	...
XX		36.4/100	33.5/100	163.4	86.4	58	163.4	81.8	59	164.8	80.8	71
XXI		27.7/100	18.4/100	207.8	5.4	...	208.8	3.3	...	...	..	...
XXII		27.8/100	28.5/100	180.4	94.5	97	182.0	96.2	107	180.2	95.7	72
XXIII		18.3/100	18.1/100	193.8	20.0	...	-201.6	21.9	...	...	..	...
XXIV		18.1/100	28.0/100	160.4	65.1	...	162.4	65.7	...	162.6	77.4	...
XXV		13.9/100	17.6/100	168.0	26.2	...	175.0	28.0	...	187.0	6.2	...

object of these treatments is to partly change the cellulose into cellulose hydrates. It is not considered advizable to increase the solubility by these methods, as a poor yield is obtained in the nitrating process and the waste acids from nitration are unduly contaminated. In addition, the stabilizing of the nitrocellulose may be difficult.

To increase the solubility of a nitrocellulose, the method of T. Chandelon may be employed.[1] It consists in heating the nitrocellulose under a pressure of 1.5–3 atmospheres in a lead-lined autoclave for a variable time in the presence of 1.5%–3% of mixture of nitric and sulfuric acids. After preliminary soaking in dilute nitric acid, the nitrocellulose is introduced into the autoclave and quickly heated to the desired pressure. During the treatment the nitrocellulose loses very slightly in weight, but the nitrogen content is not appreciably changed. The solubility figure is greatly increased from an average of 18.25% to an average of 28.88%. Nitrocellulose which is almost completely soluble in ether-alcohol mixtures, gives solutions of greatly decreased viscosity after digestion for 1.5 hours at 30 lbs. pressure with 1.5% acid. The strength and elasticity of the filaments from treated nitrocellulose is greater than that of filaments from untreated nitrocellulose. The changes undergone by nitrocellulose under the pressure-boil are probably physical rather than chemical. They are not permanent and the solubility may be reduced to the original figure before treatment if the material is allowed to stand for one year in a moist condition in the absence of light.

From published data, and as the result of his own researches, H. Schwarz[2] corroborates that the solubility of various kinds of nitrocellulose is greatly influenced by the purity and mode of preparation of the nitrocellulose, and the purity of the solvents employed, and he finds that in particular, while the solubility in boiling absolute alcohol was high, it rapidly decreased when water was present, becoming practically zero for 88% alcohol. Similar results were obtained with cold alcohol. Commercial alcohol gave somewhat higher results probably owing to the impurities present. Experiments are also described showing the influence of the time of nitration of the cellulose. The solubility first rises with increased time of nitration, then fluctuates and finally falls.

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[1] E. P. 11941, 1911; abst. C. A. 1912, **6**, 3183; J. S. C. I. 1912, **31**, 303. F. P. 429750, 1911; abst. J. S. C. I. 1911 **30**, 1281; Kunst. 1912, **2**, 16. D. R. P. 255067; abst. C. A. 1913, **7**, 1291; Wag. Jahr. 1912, **58**, I, 429; Chem. Zentr. 1913, **84**, I, 363; Chem. Ztg. Rep. 1913, **37**, 36; Zts. ang Chem. 1913, **26**, II, 149; Zts. Schiess. Spreng. 1913, **8**, 61. Belg. P. 225909, 1910. Kunst. 1913, **3**, 104; abst. C. A. 1913, **7**, 1969.

[2] Caout. et Gutta. 1914, **11**, 7964, 7967, 8199, 8359; abst. J. S. C. I. 1914, **33**, 744; C. A. 1914, **8**, 421, 571; J. C. S. 1914. **106**, I, 1053; Koll. Chem. Beihefte, 1914, **6**, 90; Kunst. 1913, **3**, 421, 445; Zts ang. Chem. 1914, **77**, II, 230, 231, 504.

In attempts to rectify alcohol containing nitrocellulose in solution (probably ethyl alcohol used in hydraulic dehydration of cellulose nitrate preparatory to gelatinization), the following observations are recorded:

1. The gelatinous mass that appears in the process of removing the alcohol by pressure, consists partly of "swollen," and partly of "dissolved" nitrocellulose.
2. The presence of acetic or nitric acids in the alcohol after distillation is due to the decomposition of certain impurities in the nitrocellulose that had been dissolved in the alcohol.
3. It is possible that a cellulose nitrite is involved. There are always impurities in nitrocellulose that cannot be completely removed by the cold water washing process alone.
4. The dehydration of nitrocellulose by means of alcohol represents also a form of stabilization of the treated material.
5. Experiments to obtain an acid-free distillate after one distillation by means of chemical "neutralizers" have not yielded satisfactory results.
6. With all neutralizers, a portion of the NO from the decomposition of the nitrocellulose escapes and is carried over by the alcohol in the distillation apparatus, so that the acid-containing distillate must be neutralized and again distilled.
7. The solubility of a nitrocellulose is strongly influenced by additions or admixtures.
8. Since the effect produced by neutralizers and their reaction products upon the solubility of nitrocellulose in the rectified alcohol can not be measured, it is recommended that careful supervision be given to the drying processes and to the rectification of the alcohol.

E. Mulder[1] has determined the solubility of guncotton in ammonium hydroxide and also in cuprammonium solutions. C.

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[1] Scheik. Onderz. 3, II; Onderz. 157; abst. Jahr. Chem. 1863, **16**, 568.

Häussermann[1] has shown that nitrocellulose dissolves at ordinary temperatures in HNO_3 of 1.473 density, but slightly. N. Stepanow[2] has investigated the influence of variation of the proportion in the case of solvent mixtures and the molecular weight of the alcohols added, as well as variations due to the presence of chloroform, benzene, toluene and phenol, in conjunction with different temperatures of the solutions.

Viscosity of Nitrocellulose. The nitrogen content bears very little relation to viscosity in a nitrocellulose, because the viscosity may be varied within comparatively wide limits in the process of esterification without a corresponding increase or diminution of the percentage of nitrogen in the nitrocotton. Therefore attempts to duplicate the viscosity of a cellulose ester solution from considerations of acid mixtures and length of cotton immersion in the bath, are futile. The viscosity is also modified to a great extent by the combination of solvents and the purity of each. Furthermore, where that decreasing solubility amounting almost to incipient precipitation is reached by the attenuation of a nitrocotton solution with a non-solvent, a pseudo-viscosity arises, whereby as the solution becomes more dilute in nitrocotton from increment of non-solvent, as the limit of solubility approaches, often the viscosity apparently is increased.

The question of viscosity—from a commercial point of view—is of great import, for bronzing liquids, pyroxylin lacquers which are either applied by dipping or by brushing, must be made to a given "flow," in order to insure best results. That is, the viscosity must be brought to a standard, while the total non-evaporable solids are not disturbed. Where articles of hardware or adornment are given a protective coating of such a lacquer or solution, if the fluid be unduly viscous, either from too much nitrocotton or from a too 'heavy" pyroxylin having been used, less of the excess lacquer will run off the surface before the lacquer "sets," and hence a given volume will show a diminished covering power, without favorable results to counterbalance.

With such a solution of too heavy viscosity, satisfactory results are not obtainable by diluting the solution to the required fluidity, for in so doing the total solids are decreased, with the result that such a nitrocotton when dried on a transparent or highly polished surface will iridesce and "rainbow up," due to the tenuity of the film, which also may be too thin for proper protection. It is for this reason that various pyroxylin manufacturers blend "batches" of high and low viscosity to obtain a combination of any desired fluidity.

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[1] Zts. Schiess. Spreng. 1906, **1**, 39; abst. Chem. Centr. 1906, **77**, I, 1196; J. S. C. I. 1906, **25**, 444; Jahr. Chem. 1905–8, II, 979.

[2] Zts. Schiess. Spreng. 1907, **2**, 43; abst. Chem. Zentr. 1907, **78**, I, 1109; C. A. 1907, **1**, 1059; Jahr. Chem. 1905–8, II, 975.

Just as it is correct to designate a cellulose nitrate as of a given nitrogen content, so also is it necessary in lacquer manufacture to produce solutions where a given weight per volume of nitrated cotton is present in a solution of stated viscosity. In the production of artificial filaments and photographic films where also solutions of known viscosity are required, the evaporated solvents are but imperfectly and partially recovered. From motives of economy, therefore, it becomes expedient to use a very fluid pyroxylin so that the minimum of viscosity with maximum of total solids present will result. In other words, so that the loss of solvent may be kept as low as possible.

In general in nitration, the fluidity is always greater with increased temperature of nitration, less so with increased time of immersion of the cotton in the nitrating bath, other factors remaining the same. And inasmuch as with rise of temperature the yield decreases, it follows that a low viscosity is obtained only at the expense of the yield, i. e., the greater the fluidity, the less obtained. The various degrees of solubility are produced according to the strength of the acids used and length of immersion of the cellulose, while the viscosity results from a manipulation of the temperature of the nitrating bath. It is quite possible to produce from the same acid mixture and same source of cellulose two samples of nitrocotton, where the one formed at a lower temperature (30°-35°) will be but half as fluid as the other sample nitrated at a higher (55°-65°) degree, amyl acetate, say, being used as the solvent in both instances. In general if the proportion of sulfuric to nitric acid is increased over 3:1, the solubility in ether-alcohol, acetone, and amyl acetate increases, while the percentage of nitrogen slowly falls, although it is impossible to foretell the degree of solubility from the nitrogen percentage alone. It is possible to occasionally produce cellulose nitrates soluble in 95% ethyl alcohol where pure nitric acid or nitric acid containing less than 10% sulfuric acid is used, their nitrogen content approximating that of octonitrocellulose (11.13% N). The commercial preparation of nitrocottons for films and lacquers is a careful adjustment of nitration conditions to embody the minimum of temperature to produce the highest yield of lowest viscosity, rather than an endeavor to obtain the greatest weight of nitrate which will merely dissolve in the solvent. In any solution where the liquids consist of both a solvent and non-solvent (amyl acetate and benzine) the viscosity increases as the point of precipitation is neared, due to preponderance of the pyroxylin non-solvent (benzine). It would appear from the literature on the subject that a mixture of 3 parts ether to 1 part alcohol is the more commonly employed solvent for technical use. This, however, is not true, amyl acetate and commercial wood alcohol (containing acetone) having practically replaced the ether-alcohol formerly used. Even in the manufacture of cinematographic and other continuous photographic films where a low evaporative solvent is required, the acetates obtained from the lower fusel oil fractions (butyl and propyl acetates) combined with wood alcohol, are being used more and more, due to their high solvent power and low moisture absorption during evaporation, thus reducing the tendency toward clouding and fogging of the films.

It has been found unusually difficult to manufacture nitrocellulose intended for blasting gelatin, because it must have a certain body within rather narrow viscosity limits, and the insoluble matter must be reduced to a fraction of 1%.

The curious observation has been made and repeatedly substantiated, that a nitrocotton solution in ether-alcohol, amyl acetate, or acetone, decreases in viscosity upon standing if the solution be slightly acid. This fact is made use of in the artificial silk industry, where, in Germany, Lehner has obtained patent protection for the expression "acid-moistened collodion." If the nitration produces a pyroxylin of higher viscosity than desirable, the solution in ether-alcohol or amyl acetate is made faintly acid usually by the addition of 0.2% acetic acid—and exposed to the light. The viscosity gradually diminishes, and when it reaches the desired point the solution is either used in the acid state or carefully neutralized by alcoholic sodium hydroxide, the sodium acetate formed being readily soluble and hence the clearness of the solution unimpaired. Although the viscosity of cellulose nitrate solutions bears no direct relation to the nitrogen content, still it reaches its maximum with the highest percentage of nitrogen. The presence of traces of acid in amyl acetate-pyroxylin solutions does not decrease the viscosity as quickly or to as great an extent as the same pyroxylin and same percentage of acid dissolved in ether-alcohol. The viscosity of solutions sinks with increase of water content in the nitrating mixture, and the yield is correspondingly lowered. Nitration of the same cotton at 20° for eight hours, at 40° for two hours, or at 60° for 15–20 minutes, can be made to produce a nitrocellulose of substantially the same solubility, but not necessarily of the same viscosity.

In the spinning of artificial filaments, the addition of varying amounts of water to the nitrocotton solutions can be made so as to obtain a series of viscosities over a wide range. For instance, J. Douge[1] specifies that the nitrocellulose must contain from 6% to 10% of moisture. J. Stoerk specifies 12% to 20% of water;[2] G. Lacroix claims to be able to spin satisfactory filaments with a nitrocellulose containing 35% to 45% of water;[3] H. de Chardonnet[4] describes the use of cotton containing 25% to 30%; while B. Julich[5] employs 21%–24%.

G. Lunge,[6] and later C. Piest,[7] have made experiments as to the influence upon viscosity which is exerted by varying the factors in the nitrating bath, and their combined generalizations, are as follows:

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[1] U. S. P. 699155, 1902. E. P. 2476, 1902. D. R. Anm. D-11841 abst. J. A. C. S. 1902, **24**, 515; J. S. C. I. 1903, **22**, 91; J. Soc. Dyers Col. 1903 **19**, 111; Mon. Sci. 1903, **59**, 6; 1905, **63**, 322; Chem. Zts. 1903, **2**, 438.

[2] E. P. 26982, 1902; abst. J. S. C. I. 1903, **22**, 1345; J. Soc. Dyers Col. 1904, **20**, 30; Mon. Sci. 1905, **63**, 322.

[3] E. P. 2192, 1905. F. P. 351265, 1905; abst. J. S. C. I. 1905, **24**, 841; J. Soc. Dyers Col. 1905, **21**, 85, 206; Mon. Sci. 1906, **65**, 37; 1907, **67**, 600; Chem. Zts. 1905, **4**, 539.

[4] E. P. 27527, 1906. F. P. 371544, 1906. U. S. P. 866768, 1907; abst. J. S. C. I. 1907, **26**, 1004; J. Soc. Dyers Col. 1908, **24**, 118; Mon. Sci. 1907, **67**, 600; 1908, **69**, 61; 1910, **73**, 297.

[5] U. S. P. 410404, 1889; abst. J. Soc. Dyers Col. 1889, **5**, 167. F. P. 188304, 1888; abst. Mon. Sci. 1888 **32**, 1260. E. P. 5270, 1888; abst. J. Soc. Dyers Col. 1889, **5**, 151.

[6] Zts. ang. Chem. 1906, **19**, 2051; abst. C. A. 1907, **1**, 908; J. S. C. I. 1907, **26**, 33; Bull. Soc. Chim. 1907, **2**, 493; Chem. Zentr. 1907, **78**, I, 947; Jahr. Chem. 1905–08, II, 981; Meyer Jahr. Chem. 1906, **16**, 323; Wag. Jahr. 1906, **52**, I, 498.

[7] Zts. Schiess. Spreng. 1910, **5**, 409; abst. Wag. Jahr. 1910, **56**, I, 494; Jahr. Chem. 1910, **63**, II, 425; Chem. Zentr. 1910, **81**, II, 1889; Chem. Ztg. Rep. 1911, **35**, 35; J. S. C. I. 1911, **30**, 50; C. A. 1911, **5**, 590. Meyer Jahr. Chem. 1910, **20**, 327. See C. Piest, Zts. ang. Chem. 1908, **21**, 2497; abst. Chem. Zentr. 1909, **80**, I, 474.

1. Where the cotton is nitrated at higher temperatures, the yield of nitrocellulose is lower, the waste acid undergoes radical changes due to the oxidizing power of the nitric acid on the cotton, so that it can be profitably rejuvenated but one or a few times, and not indefinitely as in ordinary practice.
2. Where the period of nitration is prolonged the viscosity is diminished, but this results in a lowering of the productive capacity of the plant, and the waste acid is correspondingly changed.
3. Where strongly bleached, mercerized or other modified cellulose is used, the viscosity is lower, and more thorough and prolonged washing of the nitrocotton is necessary in order to bring the product to the prescribed standard of stability.
4. Where mineral acids are added to the pyroxylin solution, the viscosity is attenuated in degree dependent upon the length of time the pyroxylin has been in contact with the acid and the temperature of the solution, and in a much lesser degree to the amount of mineral acid present.
5. Where glacial acetic acid is added to the nitrocotton in solution, the action is similar to (4), except that the action of the acid is much less pronounced from the point of reducing the viscosity.
6. Liberal washing and boiling of the nitrocellulose and a high degree of stability are conducive to the production of a collodion of relatively low viscosity.

All nitrocellulose solutions when exposed to sunlight for any considerable length of time throw down a slight deposit, and the viscosity of the solution diminishes correspondingly.

According to C. Piest[1] the diminution in viscosity when nitrocellulose solutions are allowed to stand for several months, is thought not to depend on increased molecular complexity, but to changes in the colloidal state of the solution due to a decrease in the size of the particles of the disperse phase. The viscosity is also lessened by impurities as acetaldehyde in the solvent, and by hydrocellulose and oxycellulose esters. He claims that the rate of filtration of such solutions may be timed and used as a check on the decrease in viscosity, but he apparently has not taken into consideration the fact that the speed of filtration of a nitrocellulose solution may be greatly hampered by small suspended particles which decrease the porosity of the filter by clogging the interstices.

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[1] Zts. ang. Chem. 1911, **24**, 968; 1913, **26**, 24; abst. J. S. C. I. 1911, **30**, 835; 1913, **32**, 132; C. A. 1911, **5**, 3153; 1913, **7**, 1284; Kunst. 1913, **3**, 92; J. Soc. Dyers Col. 1913, **29**, 194; J. C. S. 1911, **100**, ii, 586; 1913, **104**, I, 250; Chem. Zentr. 1911, **82**, II, 358; 1913, **84**, I, 1411; Meyer Jahr. Chem. 1911, **21**, 220; Wag. Jahr. 1913, **59**, II, 543.

It is a fact that the heavier the nitrocellulose solution, the more the viscosity is lowered by the addition of a nitrocotton of lower viscosity, as compared with the calculated viscosity of the mixture. In general, an ether-alcohol solution is more viscous than an acetone solution of the same nitrocellulose.

G. MacDonald[1] accounts for the variable viscosity in one and the same solution by the action of light. He found that in diffused daylight a solution of collodion-cotton in acetone diminished in viscosity one-half upon standing for seven days, while the same solution in the dark diminished but little.[2] O. Guttmann[3] has confirmed the results of Piest that the viscosity of strongly bleached nitrocottons is much less. H. Schwarz[1] has pointed out that solutions of nitrocellulose in alcoholic camphor are more viscous than ether-alcohol solutions, the latter in turn being more viscous than acetone solutions. In the first case, the viscosity is lower than solutions of higher camphor concentrations. His results have shown that determinations of viscosity of solutions of nitrocellulose in alcoholic camphor during heating to 60°, indicate that the variation in viscosity upon heating is reversible. Additon of 1% urea to alcohol-camphor solutions of nitrocellulose causes an increase of 10%–15% in viscosity, but further additions had no effect.

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[1] J S. C. I. 1911, **30**, 251; abst. Zts. Schiess. Spreng. 1911, **6**, 389; Chem. Zentr. 1911, **82**, I, 1902; Meyer Jahr. Chem. 1911, **21**, 340

[2] He found in mixing solutions of low and high viscosity respectively, that the more viscous the solutions the more the viscosity was lowered beyond the calculated viscosity of the mixture. Mixtures of solutions of different strength of the same nitrocellulose in the same solvent, possessed viscosities differing little from the calculated values. In general, nitrocellulose solutions become less viscous the more the cotton used has been bleached and the higher its copper number. These results indicate that the fall of viscosity is due to the presence of impurities, such as esters of oxycellulose. The impurities in question are derived from the "β-oxycellulose" formed during bleaching, etc., this name being a collective one for all the products soluble in sodium hydroxide solution. Normal cottons contain similar oxidation products, but to a smaller amount. The experiments described by the author show that treatment of cellulose with oxidizing agents, acids, and strong alkali solutions, in each case yields products soluble in dilute alkali solutions (oxycellulose, hydrocellulose, and alkali-cellulose, respectively), which have acid properties, and vary in composition according to the strength and nature of the reagent. They are precipitated from the alkali solutions by the addition of acids. The residue undissolved by the alkali (α-oxycellulose, α-hydrocellulose, α-cellulose) must be regarded as unaltered cellulose, which however, retains small quantities of the "β-" products.

[3] Zts. ang. Chem. 1909, **22**, 1717; abst. Jahr. Chem. 1909, **62**, II, 388; C. A. 1910, **4**, 109; J. S. C. I. 1909, **28**, 1007; Bull. Soc. Chim. 1909, **8**, 222; Chem. Zentr. 1909, **80**, II, 1285; Meyer Jahr. Chem. 1909, **19**, 335; Wag. Jahr. 1909, **55**, II, 431;

F. Baker[2] has summarized and extended the work of Bruley,[3] A. Lehner,[4] E. Berl and R. Klaye,[5] and E. Berl,[6] on the viscosity of cellulose nitrate solutions, in a study of the relation between viscosity and chemical constitution, and has pointed out, that in conducting a research of this nature, the nitric esters of cellulose present certain very definite advantages over the majority of colloids from the viewpoint of an investigation into the physical properties of their solutions. His object was to establish a quantitative relation between the concentration and viscosity of solutions of cellulose nitrates, and to examine the effect of varying the solvents employed.

In examining the viscosities, solutions not exceeding a concentration of 2% were mostly employed, and in the solvents as stated. The nitrocelluloses used were selected samples of products prepared on a large scale, viz., (a) blasting nitrocellulose, as used in the manufacture of blasting gelatin, 11.85% N, completely soluble in ether-alcohol; (b) highly soluble nitrocellulose, as used in ballistite, 12.38% N, solubility in ether-alcohol 97.4%; (c)

[1] Zts. Chem. Ind. Koll. 1913, **12**, 32; abst. J. S. C. I. 1913, **32**, 191; C. A. 1913, **7**, 2304; 1915, **9**, 3128; J. C. S. 1913, **104**, ii, 189; Chem. Zentr. 1913, **84**, I, 1635; Wag. Jahr. 1913, **59**, II, 593; Zts. ang. Chem. 1913, **26**, II, 407; Mon. Sci. 1915, **82**, 49.

[2] J. C. S. 1913, **103**, 1653; abst. C. A. 1913, **7**, 4069; J. S. C. I. 1913, **32**, 991; Bull. Soc. Chim. 1913, **14**, 1475; Chem. Zentr. 1913, **84**, II, 1855.

[3] Mem. Poudres et Salpetres, 1895–96, **8**, 111.

[4] Zts. ang. Chem. 1906, **19**, 1583; abst. Chem. Centr. 1906, **77**, II, 1369; Wag. Jahr. 1906, **52**, II, 394.

[5] Zts. Schiess. Spreng. 1907, **2**, 381, 403, abst. C. A. 1908, **2**, 184; J. S. C. I. 1907, **26**, 1157; J. C. S. 1908, **94**, I, 504; Chem. Zentr. 1908, **79**, I, 1381; Chem. Ztg. Rep. 1908, **32**, 43; Jahr. Chem. 1905–08, II, 976.

[6] Zts. Schiess. Spreng. 1909, **4**, 81; abst. C. A. 1909, **3**, 1926; J. S. C. I. 1909, **28**, 380; Chem. Zentr. 1909, **80**, I, 1275; Jahr. Chem. 1909, **62**, II, 384; Meyer Jahr. Chem. 1909, **19**, 335; Wag. Jahr. 1909, **55**, I, 431.

guncotton prepared for the manufacture of cordite, 12.98% N, solubility in ether-alcohol 9.6%. The solvents were acetone, ethyl formate, methyl, ethyl, propyl and amyl acetates, ethyl butyrate, acetoethyl-*o*-toluidide, ethyl-*o*-tolylethylcarbamate, ethyl phthalate, alcohol-ether, methyl alcohol-ether, benzylalcohol ether, and methyl alcohol-anisole. The ethyl-*o*-tolylethylcarbamate (tolylethylurethane) was prepared by the action of ethyl-*o*-toluidine on ethyl chloroformate; it is a colorless oil boiling at 257° at 755 mm. Phenylethylurethane (b. p. 249° at 760 mm.) was prepared in a similar way. Both compounds readily dissolve the "soluble" kinds of nitrocellulose. The viscosities were determined in a series of viscometers of the Ostwald-Poiseuille type and the results are given in tables. The variation of viscosity with the concentration of the solution is shown to follow the law $n = n_0(1 + ac)^k$, where n and n_0 are the viscosities of the solution and the solvent respectively c is the concentration and a and k are constants depending on the nature both of the solute and the solvent. For comparing different solvents the value of $\frac{d \log n}{dc}$ was found most convenient. The variation of this constant with different solvents, using the same nitrocellulose, indicated that the better the solvent the lower the viscosity of the solution. The nitrocellulose prepared from the mercerized celluloses have a much lower viscosity than those from normal cellulose, and the similarity of the viscosities of cuprammonium solutions of mercerized cellulose and normal cellulose respectively, observed by H. Ost[1] cannot be due to chemical identity of the two products, as suggested by him, but probably due to a change in normal cellulose preceding or accompanying its solution in cuprammonium.

The results of Baker are summarized on page 1737.

H. Nishida[2] has investigated the viscosity of nitrocellulose in alcoholic camphor, and summarizes his work as follows:

1. Unstable cellulose nitrates, and those containing free acid

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[1] Zts. ang. Chem. 1911, **24**, 1892; abst. J. S. C. I. 1911, **30**, 1247; C. A. 1912, **6**, 684; J. C. S. 1911, **100**, i, 838; Chem. Zentr. 1911, **82**, II, 1519; Chem. Ztg. Rep. 1911, **35**, 520; Meyer Jahr. Chem. 1911, **21**, 220; Wag. Jahr. 1911, **57**, II, 428.

[2] Kunst. 1914, **4**, 81, 105; abst. Caoutchouc et Gutta, 1914, **11**, 8103, 8200; J. S. C. I. 1914, **33**, 476; C. A. 1914, **8**, 2061; Wag. Jahr. 1914, **60**, II, 466; Zts. ang. Chem. 1914, **27**, II, 391.

TABLE CXXI —VISCOSITY OF NITROCELLULOSE SOLUTIONS

Solvent	Solute	Density	Viscosity	*a*	*k*	*ak* from Curve
Acetone at 25°	Blasting soluble N/C	0.7881	0.003151	1.024	6.8	6.22
Acetone at 15°	Blasting soluble N/C	0.7995	0.003441	1.024	6.8	6.72
Acetone at 25°	Highly soluble N/C	0.7881	0.003151	0.4725	6.8	3.22
Acetone at 15°	Highly soluble N/C	0.7995	0.003441	0.4755	6.8	3.33
Acetone at 0°	Highly soluble N/C	0.8146	0.003979	0.505	6.8	3.41
Acetone at 25°	Guncotton	0.7881	0.003151	0.5905	6.5	3.73
Ethyl formate at 25°	Blasting soluble N/C	0.9164	0.00389	....	..	7.97
Methyl acetate at 25°	Blasting soluble N/C	0.9213	0.00391	....	..	6.98
Ethyl acetate at 25°	Blasting soluble N/C	0.8948	0.00432	1.024	8.78	8.52
Ethyl acetate at 15°	Blasting soluble N/C	0.9070	0.004825	....	..	8.92
Propyl acetate at 25°	Blasting soluble N/C	0.8837	0.00555	1.024	9.06	8.77
Amyl acetate at 25°	Blasting soluble N/C	0.8663	0.008075	1.024	9.19	9.37
Ethyl propionate at 25°	Blasting soluble N/C	0.8848	0.005076	....	..	9.00
Ethyl butyrate at 25°	Blasting soluble N/C	0.8744	0.006253	....	..	9.65
Acetoethyl-*o*-toludide at 25°	Blasting soluble N/C	1.0082	0.0995	....	..	6.03
Ethyl *o*-tolylethylcarbamate at 25°	Blasting soluble N/C	1.0225	0.09403	....	..	10.45
Ethyl phthalate at 25°	Blasting soluble N/C	1.1142	0.1006	....	..	7.72
Ethyl acetate at 25°	Highly soluble N/C	0.8948	0.00432	....	..	4.61
Ethyl acetate at 15°	Highly soluble N/C	0.9070	0.004825	...	..	4.79
Ethyl alcohol 50 per cent., ethyl ether 50 per cent.	Blasting soluble N/C	0.7541	0.004709	....	..	7.41
Ethyl alcohol 25 per cent., ethyl ether 75 per cent.	Blasting soluble N/C	0.7335	0.003128	....	..	7.50
Methyl alcohol 50 per cent., ethyl ether 50 per cent	Blasting soluble N/C	0.7564	0.003845	....	..	6.03
Benzyl alcohol 50 per cent, ethyl ether 50 per cent.	Blasting soluble N/C	0.8979	0.009867	....	..	8.53
Methyl alcohol 50 per cent, anisol 50 per cent	Blasting soluble N/C	0.8923	0.007054	....	..	6.28

show considerably lower viscosities in camphor-alcohol solution.

2. Organic bases increase the viscosity.

3. Solvents other than camphor and camphor substitutes lower the viscosity.

4. It is significantly decreased by a rise in temperature of the solution.

5. Stirring, or the passage of an electric current increases the viscosity.

6. The effect of the addition of inorganic salts is relative; however, there exists within the cations and anions a certain "chain-effect" (Wirkungskette).

7. Long standing has no effect after the expiration of a definite time.

8. Additions of oil slightly raise the viscosity.

9. Aromatic acids generally lower it, while fatty acids raise it.

10. Phenol generally increases the viscosity.

11. Hot washings after the removal of the free acid increases solubility and diminishes viscosity.

12. Nitration of long duration generally yields a less viscous nitrocellulose, and the same is true of higher nitration temperatures, which also influences the yield of nitrocellulose.

13. Water in the nitrating acids exerts a distinct influence upon the viscosity, a content of 18% giving best results.

14. More important is the ratio of nitric to sulfuric acids in the mixed acids; 25:35 gives nitrocellulose of the highest viscosity.

15. The nitrogen content of the prepared nitrocellulose showed no relation to the viscosity.

16. Bleaching often lowers the viscosity due to the formation of oxycellulose.

17. After treatment with metallic salts often influences the viscosity, while stabilizers increase the same.

18. The lower the moisture, the higher the apparent viscosity.

19. The viscosity of a mixture of two different nitrocelluloses can be approximately calculated by a formula given.

R. Fric[1] makes use of the measurement of the viscosity or rate of flow of an acetone solution of nitrocellulose, to determine he changes affected by storage. G. Cahen[1] diminished viscosity y the addition of aluminium chloride and sodium formate. itanine, Ltd., and P. Bowles[2] find the addition of a small amount f boric acid is advantageous to retain the viscosity in cellulose ster solutions, especially the acetate.

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[1] Compt. rend. 1912, **154**, 31; abst. C. A. 1912, **6**, 2531; J. C. S. 1912, **102**, i, 73; J. S. C. I. 1912, **31**, 92; Bull. Soc. Chim. 1912, **11**, 820; Chem. Zentr. 1912, **83**, I, 694.

According to O. Carlsson and E. Thall,[3] the viscosity of solutions of nitrocellulose, acetyl-cellulose, celluloid, and other cellulose esters, is permanently reduced by heating the solutions, while preventing the escape of solvent, to a temperature between 60° C. and "the temperature at which the ester in question is decomposed." The temperature to which the solution is heated and the duration of the heat are correlated; the longer the heating and the higher the temperature, the more is the viscosity reduced.

With cellulose acetate, and in a more erratic measure with cellulose nitrate, the viscosity of a solution of the same cellulose ester will increase with the molecular weight of the solvent in an alkyl-ester of a fatty acid, i. e., methyl acetate will produce the lower viscosity (give the lightest flow), as compared with (say) amyl acetate. This statement in the author's experience, has been repeatedly experimentally verified. Furthermore, the addition of resins (shellac, mastic, dammar, sandarac, copal) to a pyroxylin solution, although the total solids per unit volume is thereby increased, the viscosity falls materially, i. e., the solutions become thinner. Celluloid solutions are less viscous upon the addition of shellac. Where a portion of the solvent in a nitrocellulose solution is replaced by non-solvent, if the latter be added in amounts sufficient to nearly bring the nitrocotton to the poin of incipient precipitation, the viscosity increases materially Heating a pyroxylin solution under pressure materially lower the viscosity, while exhausting the air from a solution at room temperatures, slightly raises the viscosity.

To any pyroxylin solution which is too viscous, the addition of a small amount of denatured alcohol—usually not more than 5%—will reduce it entirely out of proportion to the bulk of alcohol added. Benzene reduces viscosity less than benzine, when added to pyroxylin lacquers in equivalent volumes. It is the author's experience that the longer stapled cottons treated under identical conditions produce more viscous nitrates than the shorter staple inferior grades. The same cotton nitrated on a clear day will give a tougher and more viscous nitrocotton than when nitrated on a heavy, damp, foggy day, other conditions remaining the same. The manipulation of cotton in the nitrating bath, afterwards in the washing and boiling processes, and finally in the judicious selection of solvents and solvent combinations, to produce solutions of pre-determined "flowable qualities" is certainly an art not to be acquired by the mere perusal of textbooks and works on the subject. It appears there is no definite connection between brittleness of smokeless powder and the viscosity of their solutions in ether-alcohol. Cotton nitrated by the displacement process can be made to give more uniformly highly viscous nitric esters, than where the centrifugal method of nitration is employed. The process of pulping in the purification of nitrated cellulose also influences to a marked degree the viscosity of the nitrocotton, decreasing the viscosity where the pulping has been carried too far.

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[1] F. P. 434868, 1910; abst. J. Soc. Dyers Col. 1912, **28**, 85; Mon. Sc 1913, **79**, 181.

[2] E. P. 136927, 1920; abst. C. A. 1920, **14**, 1227. They find the preferred amount of boric acid to be used should be slightly more than sufficien to form a mono-borate with any alkali that may be present, a proportion o about 0.25% of the weight of the varnish having been found suitable Amounts up to 1% are said not to be harmful, but to possess no advantage The process of D. Sutherland (Can. P. 195559, 1920) is similar. The Britis Aeroplane Varnish Co. and J. Ward (E. P. 129033; abst. C. A. 1920, 1 852) employ citric and tartaric acids for the same purpose.

[3] E. P. 136141, 1920; abst. C. A. 1920, **14**, 1219.

Such is the influence of the physical form of the fiber on the process of nitration, that when flax, ramie and cotton fibers are nitrated in compartments of the *same* bath, the viscosity of the nitrated product in ether-alcohol, amyl acetate or acetone, is greatest with ramie, lower with flax, and least with cotton. By nitrating the first two at a higher temperature than the cotton, the viscosity of all three can be made substantially equal, but the yield of ramie and flax decreased. The collodion viscosity data of T. Chandelon[1] contains but little that is new.

The viscosity as well as the solubility is often materially modified by the presence of small amounts of moisture in either the cellulose nitrate or the solvents. For instance, the addition of small amounts of water (a cellulose ester non-solvent) to an

[1] Kunst. 1914, **4**, 4; abst. Bull. Soc. Chim. Belg. 1914, **28**, 24; Chem. Zentr. 1914, **85**, I, 1315; C. A. 1914, **8**, 1506; J. S. C. I. 1914, **33**, 222; Wag. Jahr. 1914, **60**, I, 358; Zts. Chem. 1914, **27**, II, 503. See also Jahr. Phot. 1895, **9**, 227.

ther-alcohol solution, will increase the solubility of the latter for itrocellulose. In this instance—and usually so—the viscosity ncreases with the solubility.

The object of the investigations of E. Higgins and E. Pitnan[1] on the viscosity of pyroxylin solutions, was the comparison f a number of commonly used types of viscosimeters, with re-pect to accuracy, facility of manipulation, and range over which hey may be advantageously used. In addition with making omparisons of viscosity with the commoner used standards, as ugar solutions, glycerol or castor oil, they have calculated abso-ute viscosities as well, in order that direct comparisons may be nade between various instruments.

Their conclusions are:

1. Outflow viscosimeters with small orifices are suitable for se with solutions of low viscosity, provided that the kinetic cor-ection and the specific gravity are considered.

2. The steel ball viscosimeter is unsuitable for use except vith solutions of very high viscosity and hence is not universally pplicable to pyroxylin solutions. It is unreliable because of the lifficulty of obtaining a uniform temperature throughout the iscous solution in the large tube, in which it is difficult to stir the olution without the formation of air bubbles.

3. The Stormer viscosimeter has apparently the greatest ange of all those examined. It has given closely checking re-ults with solutions varying in viscosity from ten times that of vater to 200 times that of castor oil at 20° C. The temperature s under control and is easily maintained constant once the point lesired is reached, since the solution is not removed from the ontainer, during the operation. By covering the container, los of volatile solvent through evaporation is reduced to a minimum Manipulation is easy and determinations can be made more rap-dly than with any of the other types investigated. It has th further advantage over outflow instruments of giving true in-stead of kinematic viscosity.

4. The importance of expressing viscosities in absolute unit is emphasized. The additional time required is slight and it expenditure is well repaid; not only are all results made of per manent value and directly comparable, being entirely independen

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[1] J. Ind. Eng. Chem. 1920, **12**, 587.

of the instrument employed, but any possible confusion between the manufacturer and the trade, which often arises due to the use of a multiplicity of empirical standards, is entirely avoided.

A further relationship has been shown by W. Gibson[1] to exist between the viscosity of cellulose solutions and the viscosity of nitrocellulose solutions. The property inherent in cellulose to which viscosity is due is transmitted to the nitrated derivative. The results indicate that high viscosity in the cellulose is accompanied by high viscosity in its derivative.

The viscosity-concentration curve for cellulose in cuprammonium has been studied, but Arrhenius's simple formula appears only to apply over short ranges of concentration.

A relationship between viscosity and solubility of cellulose in cuprammonium solution is indicated by observations made with a variety of celluloses.

The unprecedented demand for nitrocellulose solvents during the recent war, and the imperative need for economy in this direction, inaugurated the idea which has now developed into a well defined tendency, to diminish as much as practicable the viscosity of cellulose esters in order to economize on solvents, i. e., to produce solutions of maximum total cellulose ester solids, that the greatest weight may be deposited on a given area with the employment of the minimum fluid portion of the lacquer or waterproofing composition. But in this economy of solvents, two points must not be lost sight of, one being that a diminution in the viscosity factor increases the cost of production, and the other that with decreased viscosity comes a corresponding decrease in tensile strength of the cellulose ester film. The question, therefore, is not entirely to produce a product of lightest flow, but to so permute the factors of diminishing viscosity, maximum yield, and satisfactory tensile strength, so that the comparative cost is also satisfactory.

The viscosity is influenced by the yield, loss of nitric acid by fuming, and in wringing, and the contamination of the waste acid by solution therein of cellulose and lower nitrated cellulosic bodies. As has been mentioned, the viscosity rapidly diminishes as the temperature of nitration increases, and with an unusually high nitrating temperature, the hydrolyzing action of the sulfuric acid becomes apparent, and may increase to such an extent as to hydrolyze the nitrated cellulose to the point where considerable passes into solution in the esterizing bath. This causes losses not only of cellulose which is dissolved, but the acid recovery is less, and the amount of acid remaining in the nitrated cellulose mechanically is usually increased, due to the semi-gelatinous nature of a portion of the nitrocotton, which inhibits the removal of spent acid during the wringing operation.

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[1] J. C. S. 1920, **117**, 479–493.

Where in film formation and pyroxylin leather manufacture where the maximum of strength and elasticity are of prime importance, the diminution in viscosity should not be carried to the point where solvent recovery is effected at the expense of tensile strength. With the advent of the successful modern solvent recovery units, this point is receiving more serious consideration. It is a question to be decided by the individual art involved, to just what extent viscosity should be diminished at the expense of tenacity of film and increase in cost of production.

According to J. Hill[1] nitrocellulose manufactured at Gretna, Scotland, from R. D. B. cotton waste is not a homogeneous substance, and is separable by sifting through a No. 20 sieve into two portions (a) and (b), as follows:

(a) The finely beaten portion constitutes about 85%, and has a lower viscosity than

(b) The coarsely beaten portion which constitutes about 15% of the entire blend, and which contains about 1.8% of nitrocotton spots or "knots," i. e., about 0.27% of knots in the entire blend. These are completely soluble in the optimum solvent, but are much less soluble in other mixtures of ether and alcohol, and may be separated from the accompanying rag by treatment with ether-alcohol in the ratio 25:75. It would thus appear that the higher viscosity of the coarse portion is due to the presence of these "knots."

He recommends that the fineness test for nitrocellulose (see Chapter XI) be superceded or supplemented by a sifting test on the following lines:

Fifty grams of dry nitrocellulose to be sifted through a No. 20 sieve, and the portion remaining on the sieve to be weighed. The result of the test to be calculated to the percentage of fine

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[1] Experimental Report No. 116 (Dornock), Nov. 26, 1918.

nitrocellulose passing through the sieve, and recorded as the "fineness number" of the nitrocotton. The above observations merit careful experimental consideration.

W. Gibson and R. McCall,[1] in connection with the gelatinization of cordite R. D. B. so extensively employed as a propellant during the past war, the gelatinization being effected by means of a mixed ether-alcohol solvent, have recorded some interesting observations in connection with the viscosity of the solutions produced, and especially upon the influences affecting the viscosity of such solutions.

They corroborated a fact already demonstrated, that when suitable conditions are chosen, the viscosity of an ether-alcohol solution of nitrocotton is a useful characteristic, and a fixed criterion. Their solutions were composed of 4 gm. nitrocellulose in 100 cc. of the solvent combination, but it was observed that the viscosity was not a constant value, but in general increased, in some instances being so viscous that when determined by the ball fall method,[2] the latter would not fall through them, the solution having jellified or gelatinized. It was always those solutions which had a jelly-like appearance that gave an abnormal rise in viscosity on standing.

In order to arrive at a better understanding of the facts they varied the ratio of alcohol to ether, other constants remaining the same, and obtained results as follows:

VISCOSITY OF 4 Gm. NITROCELLULOSE (12.2% N) IN 100 CC. OF ETHER-ALCOHOL

Ratio Ether: Alcohol (Vol.)	Viscosity (Time in Secs.)
80:20	160.7
75:25	59.6
70:30	39.9
60:40	28.8
50:50	23.1
45:55	26.1
40:60	30.5
30:70	90.4

When the above results are plotted on a graph, it is see that the minimum viscosity value is obtained when the ratio ether to alcohol is approximately 55:45 by volume, or abo 1.1 to 1 by weight. As the ratio of ether to alcohol is increase or decreased, the viscosity rises until it reaches a maximum

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[1] J. S. C. I. 1920, **39**, 172-T.

[2] W. Gibson and L. Jacobs, J. C. S. 1920, **117**, 473.

80: 20 on the one hand, and 30: 70 on the other. With ratios outside these limits the nitrocotton was not dissolved. The optimum solvent for the cellulose ester was that containing ether-alcohol in the proportion 55: 45 by volume, gel formation taking place to a greater or lesser extent according as the solvent used was removed from, or approached that composition. The solutions obtained with the 80: 20 and 30: 70 solvents had a decidedly jellied appearance. The time of falling of the ball increased in all instances on the standing of the mixtures. The values recorded are those obtained from the first ball dropped after the solution shaken over night, had stood for 1 hour at 20°.

In one instance where a solvent rich in alcohol was employed, the time of the ball fall changed in the manner shown in the following table:

TABLE CXXIV.—ALTERATION OF VISCOSITY WITH TIME

Period. Initial (Mins.)	Viscosity, Time of Fall (Secs.)
15	102 5
18	112 2
21	117.0
26	123.7
70	167.5
101	230.0
370	801.0
550	Very long

In another instance, with a solvent rich in ether, the time of fall of the ball increased from an initial value of 557 sec. to a fall of 619 sec. in a period of 8 hrs. at 20°.

In order to ascertain to what extent the viscosity ether-alcohol curve would be influenced by variations in concentration, the viscosity curves of 3%, 5% and 6% solutions were submitted to examination with results as follows:

Ratio Ether: Alcohol (Vol.)	Viscosity (Time in Seconds)		
	3 Gm.*	5 Gm.*	6 Gm.*
90:10	130 2	.....	.....
80:20	21.1	.....	.....
70:30	10.8	170	.....
65:35	.....	92.0	.....
60:40	9 2	76.4	260.4
55:45	.....	76.5	250
50:50	9.3	78.5	260
45:55	.....	85.0	299
40:60	10.6	110	.....
30:70	13.8	.....	.....

Weight of nitrocellulose per 100 cc. of ether-alcohol.

The following table records the relation between concentration of nitrocellulose and optimum solvent:

Concentration of Nitrocellulose Solutions		Viscosity	
Gm. per 100 Cc.	Gm. per 100 Gm.	(Sec.)	Log T
3	3.93	9	0.9542
4	5.22	24	1.3802
5	6.55	76	1.8808
6	7.86	250	2.3979

S. Arrhenius[1] obtained a quite similar relationship from measurements of the viscosities of nitrocellulose in acetone solution of F. Baker.[2] Arrhenius' formula, which has some theoretical foundation, may be expressed: $\log \eta = \theta C - \log \eta_0$, where η and η_0 are the viscosities of solution and solvent respectively and C is the concentration of the nitrocellulose; θ is a number which proved to be approximately constant for a narrow range of concentrations.

In order to determine to what extent viscosity was effected by nitrogen content in the nitrocellulose, the following results were obtained:

Ratio. Ether: Alcohol (Vol.)	Viscosity (Secs.) of Nitrocellulose with	
	12.55% N	11.8% N
90:10	....	Very long
80:20	Very long	198
75:25	12.9	.....
70:30	7.6	45
65:35	8.5	.....
60:40	9.0	34.6
50:50	17.2	32.2
40:60	Very long	33.2
30:70	....	37.6

The following are the conclusions drawn by these investigators:

‘1. With a given nitrocellulose, the viscosity of its ether-alcohol solution is dependent upon the ratio of ether to alcohol, and reaches a minimum value at a definite ratio. On either side of this optimum ratio the viscosity rises with increasing steepness.

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[1] Biochem. J. 1917, **11**, 112; abst. C. A. 1917, **11**, 3147; Medd. K. Wetenskapsakad. Nobelinst. 1916, **3**, 13; No. 20; abst. J. C. S. 1917, **112**, ii, 130; C. A. 1917, **11**, 2635; 1918, **12**, 1355. See also A. Einstein, Ann. Phys. 1906, (4), **19**, 289; 1911, **34**, 591; abst. C. A. 1911, **5**, 2995. M. Bancellin, Compt. rend. 1911, **152**, 1382; Zts. Chem. Ind. Koll. 1912, **9**, 154; abst. C. A. 1912, **6**, 1250.

[2] J. C. S. 1913, **103**, 1653; abst. C. A. 1913, **7**, 4069; J. S. C. I. 1913, **32**, 991; Bull. Soc. Chim. 1913, **14**, 1475; Chem. Zentr. 1913, **84**, II, 1855; Meyer Jahr. Chem. 1913, **23**, 536.

2. Within the limits studied, the optimum ratio of ether to alcohol does not depend upon the concentration of nitrocellulose in solution, but is a characteristic property of the individual nitrocellulose, and its determination may be repeatedly made with concordant results. It appears the nitrogen content is the governing factor.

3. The minimum viscosity of a given nitrocotton sample reached in the solvent of optimum concentration is again a definite and characteristic property, although the value of this minimum viscosity is greatly affected by the origin and treatment of the nitrocellulose, and thus the determination of this minimum affords a useful check on the uniformity of manufacture.

I. Masson and R. McCall[1] in elaboration of the work on the viscosity of sols of "soluble" nitrocellulose in ether-alcohol mixtures of Gibson and McCall as above outlined, have mainly investigated mixtures of nitrocellulose with acetone, pure and aqueous, as of interest from the viewpoint of their behavior as typical colloidal solutions and suspensions.

For the experiments with dry nitrocellulose in anhydrous acetone, it was found necessary to dry the solvent by prolonged contact with calcium chloride, followed by fractional distillation with exclusion of water vapor, owing to the marked effect of traces of moisture on viscosity.[2] They found that in order to obtain consistent results, the mixtures must be made up with the aid of vigorous initial agitation followed by mechanical shaking until uniformity of composition is ensured, it being found there is a slow decrease in viscosity with time. Whereas Gibson and McCall found with ether-alcohol sols a much more rapid effect in the opposite direction, Masson and McCall determined with acetone—either anhydrous or aqueous—that the viscosity rapidly rises within a few minutes of mixing, to a maximum value, which then gradually falls, and this was found to hold true with the particular mixture of ether and alcohol in which the nitrocellulose has its lowest viscosity. However, the more widely the composition of this solvent deviates from this optimum value, the longer is the time required to arrive at its maximum viscosity.

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[1] J. C. S. 1920, **118**, 819.

[2] Attention is called to the fact that the crystalline compound formed between acetone and calcium chloride (see G. Frankforter and L. Cohen, J. A. C. S. 1914, **36**, 1103) which is soluble in anhydrous acetone, has a marked effect in the coagulation of nitrocellulose sols. Thus acetone rendered anhydrous over calcium chloride, but separated by it from filtration alone, formed with 5% of nitrocellulose a stiff jelly having an apparent viscosity of 5000 C. G. S. units, whereas when separated from the calcium chloride by distillation, the acetone gave a mobile sol, the viscosity of which was 13 units. The presence of a small amount of water largely counteracts this coagulating effect, from which it appears that hydrated calcium chloride differs from the acetone compound in this respect.

It would appear that two processes are at work in this connection, first, the absorption of solvent by nitrocellulose accompanied by the dispersion of the resulting gel, and second, a change in the already dispersed gel to which may probably be ascribed a change in the aggregation state of the particles, although not necessarily accompanied by any observable alteration in percentage composition. With acetone, and with ether-alcohol near the optimum, the former process is very rapid, while with other ether-alcohol mixtures the absorption of solvent with resulting swelling of the particles and decrease in the volume of the surrounding fluid continues for some time, even after the primary dispersion has taken place. In all cases, the second process is very slow.

Measurements were made at 20° of the viscosities of a number of kinds of nitrocellulose in acetone to which varying proportions of water had been added, the absolute viscosities in concentrations in grams per 100 gm. of acetone and water being given in the table below, the italicized numbers showing minimum viscosities.

Percentage	N = 12.3 Per cent.				N = 13.0 Per cent.		
of Water	**5**	**7**	**8.5**	**10**	**5**	**7**	**10**
0	...	....	.....	...	12.5	....	.....
1	34.2	213.2	.....	...	8.8	32.0	232
2	....	.....	.....	451	....	26.4	.....
3	11.7	62.5	157.3	...	6.1	....	110
4	....	.....	.....	218	6.0	20.8	96.4
5	8.6	41.4	90.5	...	6.0	....	83.3
6	8.2	36.7	74.6	164	*5.9*	*20.2*	81.1
7	8.0	33.8	73.8	154	*5.9*	20.7	*79.3*
8	*7.9*	32.9	72.5	144	*5.9*	21.4	79.7
9	*7.9*	*32.7*	*69.3*	138	....	23.0	83.3
10	8.1	35.5	71.4	*138*	6.6	24.6	.....
11	8.0	.....	72.7	147	....	....	94.9
12	....	36.6	75.7	...	7.3	28.2	103
13	9.1	.....	79.9	163	7.1*	....	120
14	....	40.2	.....	...	....	....	.....
15	8.6	.....	.....	154*	....	....	.....
16	....	47.6*	.....	...	....	....	.....

*Miscibility incomplete.

From the above table it will be noted that the viscosities in anhydrous acetone are relatively very high, whereas traces of water have a marked effect in diminishing viscosity, the influence of the water diminishing with further addition, until in still more aqueous mixtures the viscosity again rises. There thus appears an optimum solvent composition at which the viscosity is at a minimum. When upwards of 12% of water is present in the acetone, the liquid no longer permits the dispersion of the nitrocellulose, but still induces gelatinization to an extent proportional to the water content.

The optimum solvent composition is not the same for all kinds of nitrocellulose, and is quite independent of concentration. With sols in pure acetone, no appreciable concentration of dissolved matter was detected by ordinary vapor pressure measurements, the disperse phase presumably consisting of particles of cellulose ester gel containing absorbed solvent.

The viscosities found at 20° in anhydrous acetone are shown in the following table:

Nitrocellulose, N = 13.0%			Nitrocellulose, N = 12.2%	
Grams Per 100 Grams of Acetone	D^{20}_{4}	Viscosity (Absolute)	Grams Per 100 Grams of Acetone	Viscosity (Absolute)
	0.792	0.0033*	.	....
0.63	0.794	0.0602*	4.43	35.5
5.05	0.814	13.9	5.05	117.0
5.68	0.817	25.1	5.68	305.0
6.31	0.820	42.7	6.31	867.0
6.94	0.823	67.8	..	...
7.58	0.827	106.7	.	....

*Determined with Ostwald viscosimeter.

They deduce that no quantitative theory can apply to the viscosity of emulsoids which does not take into account the fact that the tangential stress, expressed by the viscosity, must in part be expended in keeping the dispersed particles deformed against the forces due either to interfacial tension (liquid emulsions) or to the internal elasticity of the particles (dispersed gels).

According to J. Duclaux and E. Wollman,[1] nitrocellulose can be divided into a number of fractions, which have widely differing viscosities in acetone solutions, by fractional precipitation from its acetone solution by means of aqueous acetone or water. By repeating this process with the extreme fractions, samples were obtained, the viscosities of which in 2% acetone solution were as 46: 1, and at one end a nitrocellulose was obtained, which in 1% acetone solution was as viscous as pure glycerol. These fractions obey the law of mixtures in so far as their viscosities are concerned, and the nitrogen content of the different fractions from one and the same operation is practically constant. A better method of separation of the fractions is probably by filtration through a series of ultra-filters. The different nitrocelluloses can best be characterized and differentiated by osmotic pressure measurements.

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[1] Bull. Soc. Chim. 1920, **27**, 414; abst. J. S. C. I. 1920, **39**, 528-A.

Hygroscopicity of Cellulose Nitrates. This phenomenon is undoubtedly intimately associated with the presence of hydroxyl groups in the cellulose molecule, and in proportion as these groups are suppressed by the introduction of negative acid radicals to form the corresponding esters, decreasing attraction for atmospheric moisture results. For instance, whereas cotton normally retains from 6%-10% of atmospheric moisture, this percentage gradually diminishes from the lower acetylated and nitrated cellulosic derivatives to those of higher acetic and nitric content.[1] It has also been generally known that the attraction for atmospheric moisture exhibited by the nitrocelluloses has an important bearing on the ballistic properties of propulsive powders of which these esters are the characteristic constituent.

The investigations of C. Beadle[2] and with O. Dahl[3] have definitely shown that in a series of nitrated celluloses in which the nitric content progressively increases, the proportion of "normal hygroscopic moisture" decreases in inverse ratio, and therefore the hygroscopicity would appear to be a function of the "unsaturated" hydroxyl radicals.

W. Will[4] has made an exhaustive study of the influence of the combined nitric groups upon the hygroscopic properties of cellulose. In order to obtain comparative results, it was found necessary to select two limits representing the two extremes of humidity at which constant equilibria were established. In view of the instability of nitrocellulose at higher temperatures, the author defines his standard of hygroscopicity as the difference between the weights of the materials when dried in an ordinary oven at 40° to a constant weight, on the one hand, and when exposed to an atmosphere fully saturated with moisture at a temperature of 25° for 24 hours, on the other hand.

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[1] Cross and Bevan, "Cellulose," 5.

[2] Chem. News, 1894, **70**, 247; abst. Jahr. Chem. 1894, **47**, 1133; Chem. Centr. 1895, **66**, I, 188.

[3] Chem. News, 1895, **71**, 1; 1896, **73**, 180; abst. Chem. Centr. 1896, **67**, I, 1227; Ber. 1896, **29**, 1139-R; Jahr. Chem. 1895, **48**, 1349; 1896, **49**, 1029.

[4] Mitt. Centralst. f. Wiss. Tech. Unters. 1904, No. 4, 1; abst. J. S. C. I. 1905, **24**, 148. Meyer, Jahr. Chem. 1904, **14**, 368. See also O. Masson, Proc. Roy. Soc. 1904, **74**, 230; abst. J. S. C. I. 1904, **23**, 1143; this volume, p. 515. See also W. Will. p. 513.

Raw cottons of different origin, cotton waste and hemp all had the same hygroscopic value of 7%-8%; purified cotton, rag-pulp and wood cellulose showed 6.4%-7% of hygroscopic moisture; jute with 10.8% and the starches with 10.6%-14.1% were considerably more hygroscopic than the celluloses. Mechanical treatment (pulping) or extraction of the waxes by ether increased the hygroscopicity of the raw cotton to nearly 10%, which may be regarded as approximately the true value for pure cellulose. Treatment with dilute acids and alkalis, on the other hand, decreased the affinity of the cellulose for water, as did also the previous superheating of the cotton above 100°.

Hygroscopicity of Nitrocelluloses. The determination of the hygroscopicity of 65 samples of nitrocellulose, prepared from a large variety of different cottons and containing proportions of nitrogen ranging from 13.21% to 8.20%, showed that the sum of the percentage of nitrogen and the hygroscopic moisture was constant in all cases, with a value of about 14.6. This constant remains unchanged by various mechanical, physical and chemical treatments, e. g., pulping, solution or gelatinization, treatment with dilute acids or alkalis, partial elimination of the nitrogen, complete denitration followed by renitration. The hygroscopic moisture was found to have no connection with the degree of solubility of the nitrocellulose in ether-alcohol, but depends solely on the percentage of nitrogen. Unstable nitrocelluloses show abnormally high values which, however, are reduced to the normal when the products are rendered stable by long boiling with water.

The accompanying diagram shows the experimental results obtained in the above determinations. The straight line A B illustrates the equation $H = 14.6 - N$, which, however, is only correct within certain limits, which comprise most of the nitrates of industrial importance. Extrapolation values are better expressed by the equation $H = \frac{334.3 - 23.65N}{31.11 - N}$ which takes account of the variation in molecular weights of the different nitrates, and in which the sum of the hygroscopicity and the nitrogen varies with the proportion of nitrogen; this equation is illustrated by the curved dotted line C D.

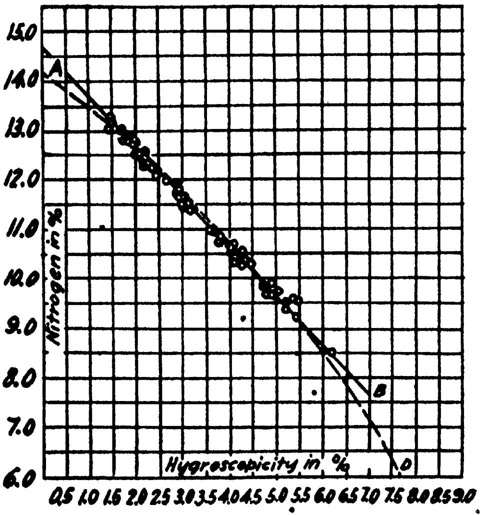

FIG. 142.—HYGROSCOPICITY OF CELLULOSE NITRATES

(a) By further drying over sulfuric acid, after drying at 40° under ordinary conditions, all the nitrocelluloses lost a further quantity of water; the sum of the hygroscopic moisture and percentage of nitrogen was then no longer a constant, but varied with the proportion of nitrogen to a greater extent. The second equation above was thus changed to $\frac{405.8 - 28.7N}{H = 31.11 - N}$.

(b) By varying the temperature at which the products were exposed to a moist saturated atmosphere from 25° to 15° and 5°, while adhering to the ordinary method of drying at 40°, the hygroscopic moisture was considerably increased, the increase being greater from 25° to 15° than from 15° to 5°. In these cases the sums of the hygroscopic moisture and nitrogen are constants within the practical limits, the equation being $H = 20-1.3\ N$ for 15° and $H = 21.6-1.4\ N$ for 5°.

(c) When the moist equilibrium was established in air of various degrees of humidity, short of saturation, an exposure of 24 hours was necessary before complete interchange was effected. It was found that the ratio between the relative humidity of the air and the hygroscopicity was only constant up to about 80% of saturation. Between 80% and complete saturation, the affinity of the nitrocellulose for moisture increased in a far greater measure than the humidity of the air. No constant relation between the percentage of nitrogen and the hygroscopicity of the nitrocellulose could be traced in air below the saturation point.

Guncotton ($N = 13\%$) as for cordite manufacture, is usually dried to a moisture-content of less than 1%. This material, if exposed to the atmosphere, absorbs water until its moisture-content varies between 1.5%-2%. The rate of absorption depends on the temperature and degree of saturation of the atmosphere. The quantity of moisture present in air-dried guncotton does not appreciably alter the rate of combustion of the nitrocellulose (compared with the rate for the completely dry material). When required for cordite manufacture it is advizable to work as near as possible to a definite moisture-content in the guncotton so as to have uniform gelatinizing effects from the acetone-water mixture. This latter mixture—from the works standpoint—is more convenient to keep at constant composition.

When a sample of dry pure nitrocellulose is immersed in water it absorbs 50% of water (on the weight of the dry material.) About 8% of moisture is absorbed in the first one or two minutes, 15%-20% of moisture is absorbed in about 5 minutes, while 25%-30% is absorbed in a quarter of an hour. No change of volume takes place by the water-absorption as the water taken up fills the capillary spaces in the fiber. The probable existence of hydrates formed by the action of water on nitrocellulose has been indicated by Haller[1] and by Chandelon.

The rate of absorption of water by nitrocellulose depends to a large extent on the presence or absence of certain substances in the ester. Thus a nitrocellulose containing a small quantity of wax or oil will generally absorb water relatively slowly. The commercial nitrocelluloses contain a small quantity of wax and oily products. If these substances are removed by ether and alcohol extraction, the dry extracted nitrocellulose is more hygroscopic than the unextracted material. The wax and the oils present in the nitrocellulose have in part come from the original cotton, and owing to their stable nature have not been removed during the nitration and subsequent purification processes. Part of the oil may also be introduced in the factory after the nitration stage.

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[1] Les. ind. Chim. 2, 420.

To increase this protective influence of waxes, and so render guncotton still less hygroscopic, E. Prentice[1] treats the guncotton in the form of fiber, pulp or granules with a solution of wax in benzoline. The impregnated guncotton is afterwards dried, when it is found that the fibers are coated with a minute layer of wax. This layer, it is claimed, prevents the fiber absorbing moisture and consequently renders it waterproof. The layer of wax also diminishes the rapidity of combustion of the explosive. The addition of oils, "paraffin tar," and similar products, have the disadvantage, according to E. Steele,[2] of reducing the explosive power and general efficiency, and in some cases the danger of spontaneous combustion is added. Instead of these compounds he prefers an alcoholic solution of nitrated resins. E. Steele's patent is claimed for explosives generally, but is particularly applicable in the case of explosives containing hygroscopic substances such as ammonium nitrate. For explosives of the latter type the process of the Societe Gen. pour la Fabrication de la Dynamite[3] is also specially applicable. Kieselguhr is added to the explosive containing the hygroscopic constituents for the purpose of absorbing any moisture originally present or subsequently taken up on storage. An example of such a type of explosive is: Ammonium nitrate (70 parts), nitroglycerol (29.1 parts) nitrocotton

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1. E. P. 2768, 1877; abst. Wag. Jahr. 1878, **24**, 466; Chem. Ind. 1878, **1**, 205; Zts. Chem. Grossgewerbe, 1878, **3**, 680; Jahr. Chem. 1878, **31**, 1138. Compare in this connection E. P. 1129, 1867; abst. Zts. Chem. Grossgewerbe, 1878, **3**, 680.

2. E. P. 4115, 1906; abst. J. S. C. I. 1907, **26**, 280; C. A. 1907, **1**, 1489; Zts. Schiess. Spreng. 1907, **2**, 195.

3. F. P. 349992, 1904; abst. J. S. C. I. 1905, **24**, 1032; Mon. Sci. 1907, **67**, 9; C. A. 1907, **1**, 1325, 1343.

(0.9 part) and kieselguhr (3 parts), all by weight.

H. de Chardonnet[1] finds that when cotton is heated in a current of dry air at 150°–170° and then nitrated a different nitration product is obtained than that which results from the nitration of the unheated cotton, and this difference shows itself in a greater solubility and lower viscosity.

The above investigations deal in the main with the study of hygroscopicity in relation to ungelatinized nitrocelluloses. N. Hansen[2] has experimentally investigated the amount of hygroscopic moisture in gelatinized nitrocellulose powders and has worked out a relation between the hygroscopic moisture and the thickness of the powder grain. The tubular or strip powder was cut in suitable lengths and the loss of weight in drying for three hours at 80° determined. Samples of varying thickness were thus dried and then exposed to the air for one year, during which period daily weighings were made. For a thickness of 0.8 mm. or greater, the moisture values follow a curve whose equation is $y = \frac{2}{\sqrt{x}}$, while for thinner grains the average moisture-content is practically constant at 2.10%. This is explained by the assumption that the moisture is not confined to the surface but penetrates to a depth of about 0.4 mm.

Density of Nitrocellulose. There is great variation to be found in the literature as to statements of the density of cellulose[3] and nitrocellulose,[4] in all probability due to the method of determination used and to the nature and freedom from moisture of the sample operated upon. H. de Mosenthal,[5] who has made a series of careful determinations of samples from various sources, gives 1.52–1.60 as the density of purified cotton, and 1.65 for that of nitrocotton.[1] The gravimetric density in the pulped state is about 0.3. It appears that nitrated celluloses of varying degrees of nitration possess practically the same densities,[2] and

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[1] D. R. P. 64031; abst. Zts. ang. Chem. 1892, **5**, 499; Chem. Centr. 1892, **63**, II, 1088; Meyer Jahr. Chem. 1892, **2**, 362; Tech. Chem. Jahr. 1892–3, **15**, 169; Chem. Ztg. 1892, **16**, 1432; 1893, **17**, 1004; Chem. Tech. Rep. 1892, **31**, II, 164; Chem. Ind. 1892, **15**, 485; Wag. Jahr. 1892, **38**, 376; Ber. 1892, **25**, 892-R; Mon. Sci. 1892, **40**, 166; Industriebl. 1892, 358.

[2] Zts. Schiess. Spreng. 1911, **6**, 461; abst. C. A. 1912, **6**, 931; J. S. C. I. 1912, **32**, 47; Chem. Zentr. 1912, **83**, I, 759.

[3] Watt Dict. Chem. **1**, 714, sp. gr. 1.27–1.45; Chemiker Kalender, **1**, 525; Cross and Bevan, "Cellulose," 1895.

[4] O. Guttman, "Schiess. und Sprengsmittelw." 1900.

[5] J. S. C. I. 1904, **23**, 292; abst. J. C. S. 1904, **86**, i, 1166; J. S. C. I. 1907, **26**, 443; J. Soc. Dyers Col. 1904, **20**, 292; 1907, **23**, 214; abst. C. A. 1907, **1**, 1770; Zts. ang. Chem. 1907, **20**, 1970; Jahr. Chem. 1905–08, II, 975; Chem. News, 1907, **95**, 189; J. S. C. I. 1911, **30**, 782; C. A. 1911, **5**, 3153; J. C. S. 1911, **100**, i, 711.

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[1] The method of determination is by means of a 100 cc. Regnault picnometer, the water being first boiled and then introduced hot after about 10 gm. of the dried material has been weighed in. The water is allowed to soak into the material, again boiled by creating a partial vacuum with the air pump in order to remove any remaining air, mechanically assisting the escape of remaining bubbles, if necessary. The failure of the water to rise in the neck of the picnometer under the bell jar of the air pump upon exhaustion, or to fall when normal pressure was again restored, was taken as an indication that all air had been removed. The results obtained are as follows:

Material Nitrated	Density of Raw Material	Nitrogen Per cent	Density of the Nitrated Material in Water
Cotton	1.607	13.5	1.665
"	1.607	13.2	1.659
"	1.607	12.95	1.672
"		12.44	1.642
"		12.37	1.681
"		12.33	1.676
"	1.607	12.30	1.654
"		12.29	1.676
"		12.27	1.666
"		11.96	1.658
"		11.36	1.669
"	1.607	11.19	1.675
"		11.10	1.653
"	1.607	10.86	1.669
Wood cellulose	1.575	13.30	1.715
" "	1.575	12.80	1.659
" "	1.575	12.52	1.673
Ramie	1.570	13.22	1.670
"	1.570	11.75	1.667*
Flax	1.548	13.15	1.685*
"	1.548	11.76	1.641

* In benzene

The above results being concordantly higher than those given by other investigators, experiments were made to determine if the apparent discrepancies could be attributable to the use of water. Determinations of cellulose made with benzene or ethyl alcohol instead of water were concordant, while with the nitrated cellulose, lower results were obtained. The failure of previous investigators to specify the method and liquid in which density determinations were made, no doubt accounts for the variation in results to be found in the literature. Disintegrated nitrated cotton gave same results as also that deposited from solution, either by precipitation or evaporation. Densities of the nitrates in solution were found to follow the normal rule that the density of a solid in solution is different from and higher than in the solid state.

[2] Viz., the increase in weight during nitration is nearly compensated

that therefore, density determinations are of little value in differentiating between the various nitrated celluloses. B. Wehrhahn,[1] gives the density as 1.66.

According to R. Escales, the specific gravity of loose guncotton in flocks is 0.1, in the pulped state 0.3, while compressed guncotton varies from 1.15 to 1.4. The absolute specific gravity of guncotton is 1.634. For blasting purposes, guncotton is more efficient the greater the density, and for such uses a density as high as 1.40 is desirable. For consideration of the influence of pressure on blasting power of guncotton, see the topic on blasting in Volume VII. For methods of determinating density of nitrocellulose, see Chapter XI of this volume.

Optical Properties. Considerable discrepancies are found in the literature as to the behavior of the various cellulose nitrates with respect to polarized light. In Muspratt Stohmann's Chemistry,[2] published in 1869, appears the statement that guncotton upon examination under the microscope in polarized light shows substantially no color, whereas cotton fiber under the same conditions of examination shows variegated colors.

G. Kindt in 1847[3] states there are distinguishable differences between guncotton and ordinary cotton when observed under the microscope under polarization in that all the fibers of crude cotton are light and show beautiful colors even where the light is greatly reduced, whereas guncotton is not so light and shows no colors or but dull ones.

M. Bonet[4] studied the decomposition of guncotton in diffused

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for by the increase in volume.

According to H. Pebenstorff (Zts. f. phys. Chem. Unterr.; abst. Chem. Centr. 1905, **76**, I, 864) the sp. gr. of nitrocellulose is 1.535 by weighing in air and in water; and 1.56 by air and by suspension in potassium iodide solution.

[1] Chem. Ztg. 1893, **17**, 1004; abst. Tech. Jahr. 1893-4, **16**, 169.

[2] See G. Lunge, J. A. C. S. 1901, **23**, 535.

[3] Pogg. Ann. 1847, **70**, 168; Berz. Jahr. Chem. **28**, 351; Jahr. Chem. 1847-8, **1**, 1137; Dingl. Poly. 1847, **103**, 214.

[4] Compt. rend. 1861, **53**, 405; abst. Chem. Centr. 1862, **33**, 512; Jahr. Chem. 1861, **14**, 712; J. prakt. Chem. 1862, **85**, 380; Rep. Chim. Pure, 1862, **4**, 15; Wag. Jahr. 1861, **7**, 517; Dingl. Poly. 1861, **162**, 137; Poly. Centr. 1861, **27**, 1519. A. Lallemand (Ann. Chim. Phys. 1871, (4), **22**, 200; abst. Jahr. Chem. 1871, **24**, 176) has measured the intensity of the polarized light given off when light is passed through collodion. C. Zakrzewski and C. Kraft (Anz. Akad. Wiss. Krakau, 1905, 506; abst. Chem. Centr. 1905, **76**, II, 1771; Bull. Soc. Chim. 1906, **36**, 437) have measured the direction taken by light rays in doubly refracting liquids while in motion, and including collodion. For investigations of A. Béchamp on the rotatory power of

light, which was evident to him by the development of red colors, the decomposition product showing light dispersions not apparent before decomposition had set in.

O. Lohse,[1] in his investigations upon the spectrum of light of exploding guncotton found the most remarkable feature to be the widening of the sodium lines, especially the more refrangible, so that in some cases the space between them is quite obliterated. This appears to have a direct relation to the violence of the explosion.

Morton Liebschütz[2] asserts his ability to recognize dodecanitrocellulose under the polarized microscope by the greater brilliancy of color, decanitrate by the true blue color, and octonitrocellulose by means of compounded colors in which the yellow strongly predominates.

According to H. de Chardonnet,[3] nitrated cotton containing up to 6.9% N may be recognized without difficulty only by a few large shrunken fibers; from 6.9% to 9.1% nitrogen there are more such fibers recognizable, and in addition a few rainbow colored ones; from 9.15% nitrogen upward, the fibers appear more uniformly gray; while from 10% to 11.28% the fibers appear as purple or dark blue, and light blue, the last color becoming more predominant as the nitrogen in the nitrocellulose increases. When all the fibers are of an equal light blue color, the polarization is said to be complete.

In a later communication, Chardonnet[4] goes into detail as to the appearance of nitrocellulose under the polariscope, including the compounds from the pentanitrate (8.32% nitrogen) to the decanitrate (12.75% nitrogen), the following conclusion being drawn:

It is stated that each nitro-compound is characterized by a

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pyroxylin, see Compt. rend. 1884, **99**, 1027; 1885, **106**, 117, 279, 368, 456; abst. Bull. Soc. Chim. 1885, **43**, 611; J. C. S. 1885, **48**, 237; Jahr. Chem. 1884, **37**, 303; 1885, **38**, 340.

[1] O. Lohse, Pogg. Ann. 1873, **130**, 641; abst. Amer. Chem. 1874, **5**, 138; J. C. S. 1875, **28**, 119; Chem. Centr. 1874, **45**, 113; Jahr. Chem. 1873, **26**, 151.

[2] Mon. Sci. 1891, (3), **33**, 119; abst. Chem. Centr. 1891, **62**, I, 517; Jahr. Chem. 1891, **44**, 2564; Chem. Ztg. Rep. 1891, **15**, 51; Chem. Tech. Rep. 1891, **30**, I, 218; Meyer Jahr. Chem. 1891, **1**, 336; Tech. Chem. Jahr. 1890–1, **13**, 170.

[3] Cf. H. Wyss-Naef, Zts. ang. Chem. 1899, **12**, 31; abst. J. S. C. I. 1899, **18**, 364; Chem. Centr. 1899, **70**, I, 458; Wag. Jahr. 1899, **45**, 944. C. Suevern, "Die Künstliche Seide," 1900, 25.

[4] Compt. rend. 1907, **145**, 115; abst. J. S. C. I. 1907, **26**, 892; Chem. Zentr. 1907, **78**, II, 1458.

different appearance in polarized light, the polariscope even being capable of differentiating the definite nitrates contained in a mixture. The relation between chemical composition and the appearance of the cellulose nitrate in polarized light remains constant, even though variations exist in the materials employed, method of preparation, diameter of fiber, and solubility in ether-alcohol. Cellulose nitrate recovered from solution in ether-alcohol or other solvent still retains its characteristic appearance in polarized light, and if partial denitration has been carried out, the lower nitrate retains the appearance characteristic of that particular step in nitration. Nitration is uniform throughout the entire thickness of the walls of the fibers. Pyroxylin, under certain circumstances, apparently contains what may be designated as water of constitution, and in these conditions the ether-alcohol solutions are less viscous and much clearer. The fibers, irrespective of the degree of nitration, always appear brilliantly yellow or white in polarized light.

L. Vignon[1] has investigated the optical activities of cellulose and nitrocellulose, using for this purpose cotton dried at 110° and nitrated by a mixture of sulfuric acid 38.95%, nitric acid 42.15% and water 18.9%, the purified product obtained in the dry state contained 10.5% of nitrogen and at a composition approximately of a dinitrocellulose (on the C_6 basis) examined under the polariscope in ether-alcohol in a concentration of 1.4943 gm. per 100 cc., showed a specific rotatory power of +19.3°, while a solution of 3.848 gm. per 100 cc. of acetone gave a rotation of +21.1°. Similar experiments carried on with cellulose thiocarbonate were inactive, due to the impossibility of obtaining sufficiently clear solutions of high concentration for accurate rotatory determinations.

H. de Mosenthal,[2] who has made careful microscopic exam-

[1] Bull. Soc. Chim. 1904, **31**, 105; Jahr. Chem. 1904, **57**, 1167; Chem. Centr. 1904, **75**, I, 651; J. S. C. I. 1904, **23**, 202. In this connection compare, A. Bechamp, Compt. rend 1856, **42**, 1213; Inst. 1856, 235; Jahr. Chem. 1856, **9**, 674; Ann. 1856, **100**, 367; J. prakt. Chem. 1856, **69**, 449; Compt. rend. 1885, **100**, 117, 279; Jahr. Chem. 1885, **38**, 340; J. C. S. 1885, **48**, 237; Ber. 1885, **18**, 113, 141; Bull. Soc. Chim. 1885, **43**, 661; Chem. News, 1884, **50**, 300; 1885, **51**, 142; A. Levallois, Compt. rend. 1884, **98**, 44, 732; 1884, **99**, 43, 1122; 1885, **100**, 456; Jahr. Chem. 1884, **37**, 302, 303; 1885, **38**, 340; J. C. S. 1884, **46**, 577, 833, 1288; 1885, **48**, 369, 500; Ber. 1884, **17**, 206, 427; 1885, **18**, 64; Chem. News, 1884, **49**, 124, 190; Bull. Soc. Chim. 1884, **43**, 83, 613.

[2] J. S. C. I. 1904, **23**, 292; Mon. Sci. 1904, **61**, 759; Jahr. Chem. 1904,

ination, depolarization, density, refraction, optical activity and dialysis of cotton, nitrated cotton, wood cellulose, ramie and flax, concludes that nitrocellulose of the same degree of nitration, dried by different methods as to temperature, acid mixture and time of immersion, shows different colors in polarized light, but the appearance differs markedly with the raw material used. According to his conclusions, dry fibers do not present the same appearance as when moistened, and the colors vary, not only with different moistening liquids, but also with the same liquid at different dilutions. They are affected by the degree of magnification, and of course appear differently, depending upon the source of the light, i. e., daylight or artificial light. That the appearance of nitrated fibers in polarized light should be a function of the method and of the degree of nitration, and that different kinds of fibers when nitrated should not be identical seems quite feasible, when it is considered that the change of color is due to changes in the anisotropic condition of the fiber brought about by physical influences, and can be entirely dependent upon chemical changes. Furthermore, samples of cellulose triacetate when examined under polarized light appeared light blue, thus closely resembling the highest nitrocellulose examined, while samples of cellulose monoacetate under similar conditions appeared brilliant, unlike any nitrocellulose fiber. However, when viewed with ordinary light the fibers appear contracted as described by Chardonnet for the lowest cellulose nitrates. The author's results confirmed the observations of Vignon that cellulose nitrate is dextro-rotatory.

The conclusion is drawn that cellulose is optically active and therefore that the cellulose must contain one or more asymmetric carbon atoms.

G. Lunge,[1] alone and in conjunction with E. Weintraub,[2] has been unable to corroborate these observations in their en-

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57, 1166; J. S. C. I. 1907, **26**, 443; C. A. 1907, **1**, 1770; Zts. ang. Chem. 1907, **20**, 1970; Jahr. Chem. 1905–8, II, 975; J. Soc. Dyers Col. 1907, **23**, 214; Chem. News, 1907, **95**, 189; J. S. C. I. 1911, **30**, 782; C. A. 1911, **5**, 3153; J. C. S. 1911, **100**, i, 711; Chem. Centr. 1904, **75**, I, 1625, 1646; 1907, **78**, II, 687, 2039.

[1] J. A. C. S. 1901, **23**, 535; Chem. Centr. 1901, **72**, II, 764; J. S. C. I. 1901, **20**, 1021.

[2] Zts. ang. Chem. 1899, **12**, 441; Chem. Centr. 1899, **70**, I, 1177, 1272; J. S. C. I. 1899, **18**, 582; Jahr. Chem. 1899, **52**, 1302. See Chem. News, 1904, **90**, 148.

tirety, but finds that the more highly nitrated celluloses appear blue in polarized light, while products with nitrocellulose percentages falling between 13.9% and 13% cannot be definitely distinguished from each other polarimetrically. While it was found that as the nitrogen percentage increased the blue color becomes less intense, but never turns gray or colorless, from observations, however, in many respects they are so conflicting as to lead them to the conclusion that the only result which can be determined with certainty was the appearance of unchanged cellulose, and this was apparent by its various strong flashes up in yellow, orange and variegated (rainbow colors), while highly nitrated products from 12.75% nitrogen upward, are distinguished by flashing up more strongly in the blue colors. Best results are obtainable by examination of the fiber moistened with 50% aqueous alcohol, or for permanent mounts, Canada balsam rendered fluid with benzene or xylene.

J. Hübner and W. Pope[1] experienced considerable difficulty in making observations, due to the transparency of the fiber, and especially in Canada balsam mounts, on account of the fact that the refractive index of cotton only differs from hard Canada balsam by 0.004.[2]

A. Trowbridge[3] has studied the optical properties of the cellulose nitrates with the object of determining whether it would prove a suitable substance with which to coat rock salt surfaces in order to preserve polished surfaces soluble in water. He found the extinction coefficient of collodion is practically negligible in the region between the visible spectrum and $\lambda = 6\mu$. In this region a rock salt plate or prism is more transparent when coated with a thin film of collodion than it is without being coated. In the region from 6μ to 10μ there are two narrow absorption bands and one extended band in the region of absorption for all of which the extinction coefficient attains values great enough to cause well-marked surface color. He finds that two strong absorption bands and one weak double one is shown. The positions of the strong bands are $\lambda = 5.89\mu$ and $\lambda = 7.79\mu$. The former of these is so narrow that it might well serve as a reference point in the infra-red spectrum.[1]

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[1] J. S. C. I. 1904, **23**, 404; abst. Jahr. Chem. 1904. **57**, 1812; Chem. Centr. 1904, **75**, I, 1625; Mon. Sci. 1906, **64**, 192; Zts. ang. Chem. 1904, **17**, 777; Wag. Jahr. 1904, **50**, II, 444. For the microscopic structure of nitrocellulose, refer to T. Bokorney, Chem. Ztg. 1896, **20**, 986; abst. Jahr. Chem. 1896, 103; Meyer Jahr. Chem. 1986, **6**, 309.

[2] The author has made nearly daily microscopical examinations of fibers in hard balsam, and finds no difficulty in obtaining clear definition, if the light is "turned low," by closing both iris diaphragms. The colored frontispiece in Guttmann "Twenty Years of Explosives," 1909, is an excellent illustration of nitrated and unnitrated cotton fiber. The structure of a nitrated cotton is rendered more distinct and stereoscopic by means of first moistening the mount with alcohol, as has been mentioned by Hartig (Untersuchungen über den Bestand und Wirkungen der explosiven Baumwolle, Braunsweig, 1847).

[3] Physical Review, 1908, **27**, 539; 1908, **27**, 282; abst. C. A. 1909, **3**, 19. See also E. Aschkinass, Wied. Ann. Phys. 1895, **55**, 401; abst. Jahr. Chem. 1895, **48**, 246. W. Julius, Verh. Kon. Akad. Wetensch. Amsterdam, 1893, Sect. I, No. 1, 49; abst. Wied. Ann. Phys. Beiblätter, 1893, **17**, 34; abst. Jahr. Chem. 1893, **46**, 158.

C. Hutchins[2] has described tests of thin films for use as windows of radiometric instruments, to avoid absorption, often of 20%, occuring in the ordinary quartz or rock salt windows. The films were made from a collodion of guncotton or celluloid dissolved in amyl acetate, by gently placing a drop of the collodion on the surface of clean water, on which it spread to a thickness when dry, of $^1/_{20}$ to $^1/_{10}$ of a wave length of light, as measured by interference or calculated from the weight, area, and density of the films. These films may be picked up on a wire ring, and are strong enough not to break from shock. The absorption of such a film at wave lengths near 10μ is less than 1%. The same collodion is also very efficient in protecting rock salt windows and silver mirrors from the action of the air without interfering with their optical properties.

J. Magnin[3] has found that when various classes of nitrocellulose and black or smokeless powder are exposed to the action of Röntgen rays for three minutes, no change is observable at the end of the irradiation period; the explosive power is not affected, and no change in composition could be detected.

These experiments were preliminary to an examination of the observations of Girard and Bordas,[4] which indicate the possibility of employing Röntgen rays in the testing of bombs and explosive shells.

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[1] He neglects to state a very important point—the percentage of nitrogen in the nitrocellulose experimented upon.

[2] Amer. J. Sci. 1912, **34**, 274; abst. C. A. 1912, **6**, 3354; Chem. Zentr. 1912, **83**, II, 1714.

[3] Anales soc. quim. Argentina, **2**, 49; abst. C. A. 1914, **8**, 3859.

[4] Annales d'hygiene, **35**, 385; abst. C. A. 1914, **8**, 3859. See Feval E. P. Appl. 15254, 1916, on preservation or reduction of depolymerizing action of light rays on cellulose esters.

D. Berthelot and H. Gaudechon[1] have made extensive investigations of the photolytic decomposition of nitrocellulose and smokeless powder by means of ultra-violet rays[2] It was found in colloiding cotton in thin quartz tubes containing mercury and of evolution of gas. The French Service powder "B" remained unaltered in appearance under the conditions of the experiments, while powders containing nitroglycerol changed in color and showed signs of exudation of nitroglycerol, and this latter phenomenon was more marked at the lower temperatures. The following tables give the composition of the gases evolved with the various powders mentioned, the results in Table CXXXI being obtained after exposure for 6 hours in an atmosphere of nitrogen, and those in Table CXXXII after the same time of exposure in an atmosphere of carbon dioxide:

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[1] Compt. rend. 1911, **153**, 1220; abst. J. S. C. I. 1912, **31**, 47; Compt. rend. 1912 **154**, 201, 514; abst. C. A. 1912, **6**, 2530; Zts. Schiess. Spreng. 1912, **7**, 52.

They exposed samples of nitrocellulose and nitroglycerol powders for six hours in thin quartz tubes to the rays from a mercury vapor lamp. In various experiments performed, the tubes containing the powders were filled with neutral, oxidizing or reducing gases. Experiments were made at 25°–28°, 40° and 70° to 75°, the powder samples being at distances of 70 to 80, 50 and 15 mms., respectively, from the lamp It was shown by parallel experiments that no gases resulted from the effect of the atmosphere alone on the powders. The decomposition resulting from the ultra-violet light proceeds in the same manner as slow decomposition normally occurring from the effects of heat, moisture, etc. The gases produced were carbon monoxide, carbon dioxide, nitrogen, nitrous oxide and nitric oxide. The absence of methane and hydrogen, which are characteristic gases of explosion, was observed. Nitrocellulose powders suffered no change in appearance but changed in color and exudation of nitroglycerol less than other powders containing that body. Nitrocellulose and nitrocellulose powders evolved carbon monoxide, carbon dioxide and nitrogen but no nitric oxide, whereas the nitroglycerol powders gave off nitric oxide in addition and also gave greater volumes of gas. The presence of an atmosphere of nitrogen did not prevent the evolution of nitrogen from the powders but in an atmosphere of carbon dioxide there was no CO_2 evolved. The effect of ultra-violet light in hastening the decomposition of smokeless powders, they claim, should be made the basis of a test for instability.

They also found (Compt. rend. 1912, **154**, 201; abst. C. A. 1912, **6**, 2530) that by exposure in thin quartz tubes containing mercury and an atmosphere of nitrogen to rays from a mercury vapor lamp, collodion cotton evolved a mixture of gases as above described containing less NO than with nitroglycerol but it also showed less stability than the French service powder which yielded no oxides of nitrogen in former tests In tests of two service powders (6 years old), one stabilized with diphenylamine and the other with amyl alcohol, the former yielded gas containing 14%, the latter 1.7% nitric oxide at 75° at 20 mm. from the source of light, while both gave no NO at a greater distance and at a lower temperature. In the first instance, decomposition was too rapid to be prevented by the presence of stabilizers. The high amount of NO, in the judgment of the investigators, probably resulted from the decomposition of the nitroso-diphenylamine formed during the six years life of the powder. The stabilized service powders gave no nitrous gases. Experiments were also conducted to determine the stability of the powder by means of the relative action of tenth normal KOH solution on the powder for a period of 30 minutes at various temperatures, the excess of alkali remaining being titrated back with acid.

[2] Service powders "B" containing no nitroglycerol, were submitted to the action of ultra-violet rays. The "B" powders were in the form of flakes, 5 mm. by 15 mm., and the cordite, ballistite, etc., were in the form of cylinders, 15–20 mm. long and 5–8 mm. in diameter. The quantities taken in the experiments were from 0.25–0.45 gm. The samples were placed in quartz tubes over mercury in atmospheres of carbon dioxide and nitrogen, and were exposed to the light from a quartz mercury lamp. The samples, kept at a temperature of from 25°–28°, were placed at a distance of from 70–80 mm. from a lamp, and in other cases at a temperature of 40° at a distance of 50 mm. The decomposition was proved to be due to the action of the ultra-violet rays, similar samples, heated at 68°–70°, showing no signs

TABLE CXXXI

	Carbon monoxide	Carbon dioxide	Nitric oxide	Nitrogen
"B" powder (1897) in amyl alcohol..............	46	23	—	31
C.G. powder (collodion cotton, dinitrotoluene and 20 per cent. nitroglycerol)	22	30	7	41
Powder containing 25 per cent. of nitroguanidine..	15	29	20	36
C_3 powder, containing nitroglycerol (25 per cent.), nitrocellulose (72), and sodium bicarbonate (3 per cent.)............	22	40	9	27

TABLE CXXXII

	Nitric oxide	Carbon monoxide	Nitrogen	Nitrous oxide
"B" powder (1903) containing 2 per cent. of amyl alcohol................	—	38	62	—
"B" powder (1909) containing 8 per cent. of amyl alcohol................	—	53	39	8
Ballistite (1889) containing 2 per cent. of aniline....	20	45	32	3
Ballistite (S.A.) containing 2 per cent. of diphenylamine................	16	48	34	2
M.D. Cordite (1906)......	26	44	26	4
A.I. powder containing nitroglycerol (25 per cent.), nitrocotton (72), and sodium bicarbonate (3 per cent.)............	27	40	29	4

It was noted that when the powders were surrounded by atmospheres of carbon dioxide that no appreciable amount of carbon dioxide was evolved during decomposition. In some instances, a slight absorption of this gas took place. The authors consider that as the French Service powder "B" does not evolve nitric oxide, under the conditions quoted in the experiments, that it is of greater stability than the propellants containing nitroglycerol.

admitting of nitration the rays from the mercury vapor lamp evolved carbon dioxide, carbon monoxide, nitrous oxide and a small amount of nitric oxide, but showed less stability than French service powder, which yielded practically no oxides of nitrogen. In subsequent investigations[1] it was found decomposition proceeded too rapidly to be prevented by the stabilizer, the high amount of NO probably resulting from a decomposition of the nitrosodiphenylamine, formed during the several years' storage of the powder.

H. Ambronn[2] has made extensive examination of nitrocelluloses of different degrees of nitration in the polarization-microscope in which he has shown that with rising nitrogen content the double refraction, at first positive, diminishes to zero, and then again increases in the negative in relation to the longitudinal direction of the fiber. With monochromatic light of wave length $435\mu\mu$ the character of the double refraction changes at about 11.8% N and at somewhat higher nitrogen contents for light of greater wave length. Examination of individual fibers showed that the nitration was uniform throughout the length of the fiber, but the several fibers in a sample of the same material sometimes exhibited differences indicating that a number of fibers were not uniform to a greater extent than others. These results, according to the author, show there is a distinct relation between the nitrogen content and the optical properties of the nitrocelluloses and indicate to him that the use of the polarization microscope should prove of great service in the nitrocellulose industry.

The color of pure nitrocellulose when ungelatinized is substantially white, but more often has a slight brown tint due to traces of iron oxide precipitated in the fibers during the various processes of washing incidental to elimination of the nitric acid, and the proper stabilizing of the cellulose nitrate. When stored in the wet condition, nitrocellulose frequently becomes dark especially upon the surface, consequent to the rapid growth of various fungi. These organisms are mostly found on the surface of the fiber of the nitrocellulose (see p. 1802).

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[1] J. S. C. I. 1904, **23**, 292; abst. Mon. Sci. 1904, **61**, 759; Jahr. Chem 1904, **57**, 1166; Chem. Centr. 1904, **75**, I, 1625, 1646. J. S. C. I. 1907, **26** 443; abst. C. A. 1907, **1**, 1770; Zts. ang. Chem. 1907, **20**, 1970; Jahr. Chem 1905–08, II, 975; J. Soc. Dyers Color, 1907, **23**, 214; Chem. News, 1907, **95** 189; Chem. Zentr. 1907, **78**, II, 687, 2039. J. S. C. I. 1911, **30**, 782; abst C. A. 1911, **5**, 3153; J. C. S. 1911, **100**, i, 711. "The important observation of H. de Mosenthal on the optical and other properties of nitrocellulose."

[2] Kolloid Zts. 1913, **13**, 200; abst. J. S. C. I. 1913, **32**, 991; C. A 1914, **8**, 422; Wag. Jahr. 1913, **59**, I, 457; Kunst. 1914, **4**, 233; Chem. Zent 1913, **84**, II, 2175.

Dissolved nitrocellulose usually gives a lower heat test. Nitrocellulose may be dialyzed, but the data available upon the dialysis and osmosis are not yet sufficiently advanced to admit of accurate generalizations.

Electrical Properties. When dry guncotton is rubbed between the fingers, especially at a moderately warm temperature, its fibers become strongly electrified and will adhere to the hand.[1] Gaiffe[2] states that when nitrocotton is rubbed in the dark sparks may be observed. The slight electrical detonations are very distinct and are especially noticeable in freshly prepared nitrocotton. In the dark a slight phosphorescence may also be observed. The electrical effect is most marked when the nitrocotton is rubbed on cat's skin.

The electrical phenomenon noticed on rubbing is intensified the more the nitrocotton is heated, the latter becoming very strongly charged with negative electricity; when the nitrocotton is near its explosive point the electrical charge is especially great.[3]

This risk of an electric charge must be taken into consideration during the "stoving" of guncotton. If the explosive is dried on wooden racks, these racks should be connected by metal strips to earth. O. Guttmann suggests that copper plates should be provided for drying, having conical apertures of $^1/_4$ mm. diameter on top and 1 mm. on the bottom, thus rendering it impossible for them to be clogged by the nitrocotton. To prevent friction, the plates may be covered with leather on the edges, and are connected with each other by metallic strips which are carried into the ground.

In addition to the electrification of ungelatinized guncotton by the passage of a current of warm air over it, there is also the possibility of nitrocellulose powders generating electricity. O. Guttmann[1] records the following instance which occurred at "Nobels" factory at Ardeer: a workman wearing rubber-soled shoes on a lead-covered floor was attending to a reeling machine, allowing strands of gelatinized nitrocellulose to pass through his right hand. In order to join a strand he dipped a finger into a bowl of acetone, when he felt a shock and a spark passed from his finger into the acetone. On experimenting, these results were always obtained under the same conditions, but when a brass nail was inserted through the sole, earthing the man through the leaden floor, nothing happened.[2] Shoes with copper rivets for similar operations have since been adopted in most explosive factories.

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[1] Plates for static electric machines have been constructed by dissolving nitrated cellulose, forming large sheets or films and pressing these together into a plate, after which they are cut or sawed into the desired shape and thickness. R. Fortun and E. Semprun (E. P. 8280, 1901) have devized a process for making separators for use in a secondary galvanic battery, by superficially nitrating sheet cardboard, and applying a coat of silicate paint to the dried surfaces. J. Fordred, Pharm. J. Trans. **6**, 318. Guthrie, Phot. News, 1880, **24**, 217; Les Mondes, 1880, **53**, 437. C. Widemann, Compt. rend. 1880, **91**, 893.

[2] Compt. rend. 1847, **24**, 88; abst. Berz. Jahr. 1849, **28**, 351.

[3] Cavalli, Oefers. af K. Vet. Akad. Forehl. **3**, 321; abst. Berz. Jahr. 1848, **27**, 418.

Meynier[3] has prepared by nitration of tissue, a product which produces sparks several cms. long, when brought near an electrophorous. The nitrated product is produced thus: Into 15 parts of a mixture of sulfuric (63%) and nitric acids (47%) is plunged 1 part by weight of tissue (such as linen, cotton or calico). The nitration is allowed to proceed for one hour. The acid is then thoroughly washed out of the fiber. The therapeutic use of such nitration products for the production of static electricity is also suggested.

In connection with the electrical properties of nitrocottons a reference may be made to the decomposition of gelatinized nitrocotton by galvanic current.[4] Collodion is a very poor conductor of electricity and only when the poles are brought very close together is a current transmitted. There is then a slight gas evolution at the negative pole, while the positive one is covered by a colorless jelly, which detonates when dry and ignited.

Not only does collodion conduct an electric current weakly,[5] but only when the poles approach to almost touching. At the negative pole there is a slight evolution of gas. It has usually been assumed that sulfur becomes negatively charged when rubbed with all other substances, just as cats fur becomes positively charged. J. Johnston[1], however, has shown that when sulfur is rubbed with pyroxylin paper it becomes positively charged, which is also the case with sealing wax and amber. The most pronounced action results when guncotton is rubbed with vulcanized caoutchouc, opposite results being obtained when the caoutchouc is rubbed with flannel. Even glass becomes strongly charged when rubbed with nitrocellulose.

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[1] "The Manufacture of Explosives," p. 60.

[2] Rept. H. M. Inspec. Explosives, 1901, 37.

[3] Compt. rend. 1848, **26**, 44.

[4] A. Brester, Arch. Neerland. des Sci. exactes et Nat. 1866, **1**, 296; abst. N. Arch. ph. Nat. **28**, 60; Zts. Chem. 1866, **9**, 690; Jahr. Chem. 1866, **19**, 84. See also Lacroix, F. P. 88026, 1869.

[5] Jahr. Chem. 1866, **19**, 88.

Physical Properties of Collodion Membranes. The usefulness of collodion membranes in osmotic and other physical experiments are becoming more fully appreciated by chemists and physicists. As far back as 1855, A. Fick[2] recognized the usefulness of collodion membranes in the study of diffusion phenomena; W. Schumacher[3] devized a method of making closed collodion sacs, with which he carried out various experiments; J. Baranetzky,[4] who has published a lengthy article on the subject, worked exclusively with collodion solutions, his results showing that cellulose nitrate films are distinguished from animal membranes, parchment paper or cellulose by a diminished permeability for saline solutions. Gorsline[5] records that peptone, albumose, albumin, starch, dextrin and certain enzymes in from 0.5%-1% solutions all dialyzed through a collodion membrane in less than twenty-four hours at a temperature of 35° in quantities sufficient to be readily recognizable. G. Malfitano[6] in filtering a colloid through collodion found that the major portion had refused to dialyze. H. Bierry and J. Giaja[7] made the discovery that pancreatic secretion having passed through a collodion membrane refused to hydrolyze starch or maltose, but that on adding a halogen electrolyte, the inhibited activity of the enzyme was restored apparently without loss of power. E. Gripon[1] found that collodion membranes reflect light and polarize it like glass both by transmission and reflection, and also that they reflect a very much larger proportion of radiant heat, for the study of which they are preferable to mica. J. Matthews,[2] who has made numerous qualitative experiments with collodion membranes, finds that they are not true semipermeable osmotic membranes, but permit the passage of solute as well as solvent, from which the author infers that when osmotic action takes place it consists of a major and a minor current in opposite directions. In experiments in which a solution is placed on one side of the membrane and a different solvent on the other, no transference was found unless at least one of the solvents is capable of wetting the membrane or the latter contains a trace of alcohol. He claims the direction and extent of the osmotic action is a question of relative solubility. S. Bigelow[3] alone, and with A. Gemberling[4] has studied the effects of forcing a pure liquid through one and the same or through different membranes at varying pressures and temperatures so as to obtain comparable numerical values. The apparatus employed consisted of a vertical glass tube, to the lower end of which was fixed a brass holder having an opening 15 mm. in diameter closed by a flat membrane of the given material held in position by means of a metal ring and screws. At right angles above the holder there was a calibrated capillary tube provided with mm. scales for measuring the volumes of liquid passing through the membranes, and some distance above this there was a stopcock in the vertical tube. The pressure was obtained and regulated by means of two mercury bulbs 10 cm. in diameter, the lower fixed in place and the other movable. In using the apparatus, the membrane holder and vertical tube were filled with water to above the stopcock, and the capillary tube nearly to the end of the scale toward the pressure bulbs, and the pressure applied by opening a stopcock in the capillary tube between the bulbs and the scale. The number of cubic millimeters which would pass through 1 sq. cm. of membrane in one minute was adopted as the unit of permeability. By means of this apparatus it was found that thin collodion membranes immersed in water gave practically the same permeability results in successive experiments; and that their permeability was not materially altered under the relatively high pressure of 840 mm. of mercury. Goldbeaters' skin showed a lower degree of permeability than collodion membranes of two or three times its thickness, while parchment paper altered continuously under constant temperatures and pressure, becoming less and less permeable. The general conclusions arrived at were that Poiseuille's law for the passage of liquids through capillary tubes applied also to the passage of water through the four membranes; and that the rate at which liquids pass through molecular interstices was capable of expression "by the same law which formulate the passage of liquids through capillary tubes."

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[1] Amer. J. Sci. 1864, **37**, 115; abst. Amer. Drug. Circ. **8**, 68; Amer. J. Pharm. **36**, 268; Proc. Amer. Pharm. Assoc. 1864, **12**, 165; Poly. Centr. 1864, **30**, 701.

[2] Pogg. Ann. 1855, **94**, 59; abst. Ann. 1857, **102**, 97; Phil. Mag. 1855, (4), **10**, 30; Jahr. Chem. 1855, **8**, 7; 1856, **9**, 15.

[3] Pogg. Ann. 1860, **110**, 337.

[4] Pogg. Ann. 1872, **147**, 195; abst. J. C. S. 1873, **26**, 346; Jahr. Chem. 1872, **26**, 28.

[5] "Contributions to Medical Research," 1903, 390.

[6] Compt. rend. 1905, **140**, 1245; **141**, 660; abst. Chem. News, 1905, **91**, 261; **92**, 237; 1906, **94**, 36; J. C. S. 1905, **88**, ii, 459; 1906, **90**, ii, 33; Chem. Centr. 1905, **76**, II, 20, 1660, 1778; Jahr. Chem. 1905-8, I, 2674, 2675, 2676.

[7] Compt. rend. soc. Biol. 1907, **62**, 432.

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[1] Compt. rend. 1875, **80**, 882; abst. Chem. News, 1875, **31**, 206; J. C. S. 1875, **28**, 726; Jahr. Chem. 1875, **28**, 118.

[2] J. Phys. Chem. 1910, **14**, 281; abst. Jahr. Chem. 1910, **63**, I, 45. J. Duclaux (F. P. 461785, 1913; abst. C. A. 1914, **8**, 2484) has described a process for purifying nitrocellulose, the impure product being subjected to dialysis, employing membranes of cellulose which possess the property of allowing dissolved impurities to pass, while retaining the nitrocellulose.

[3] J. A. C. S. 1907, **29**, 1675; abst. Chem. Zentr. 1908, **79**, I, 1132; C. A. 1908, **2**, 750; J. C. S. 1908, **27**, ii, 88; J. S. C. I. 1908, **27**, 93; Bull. Soc. Chim. 1908, **4**, 962; Jahr. Chem. 1905–8, I, 167.

[4] J. A. C. S. 1907, **29**, 1576; abst. Chem. Zentr. 1908, **79**, I, 322; C. A. 1908, **2**, 618; J. C. S. 1907, **92**, ii, 933; Bull. Soc. Chim. 1908, **4**, 747; Jahr. Chem. 1905–8, I, 167.

As the result of an examination of the enzymes, pepsin, trypsin, rennet, steapsin, ptyalin, emulsin and takadiastase, A. Porter[1] has found that all of them, with the exception of the last named, become inactive in contact with a collodion membrane. Except in the case of ptyalin, an anti-enzymic power is developed, which is specific, being limited to preventing the action of the enzyme from which it was produced. Stomach extracts rendered inactive in this way, however, prevent the action of pepsin, trypsin and rennet. Water does not extract from the collodion membrane any substance having this property, which is also shown, though in less degree, by gelatin, reed, and white of egg membrane. The formation of anti-enzyme is less, the purer the enzyme taken.[2]

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[1] Biochem. Zts. 1910, **25**, 301; cf. H. Bechhold, Zts. physik. Chem. 1907, **60**, 257. For the effect of collodion membranes on saponin, solanine, and the haemolytic glucoside found in *Amanita phalloides*, see W. Ford, J. Pharmacol. 1910, **1**, 269.

[2] Authors who have worked in this field and observed, have failed to record the great variations in permeability of collodion membranes in the following two particulars: (1) The same cellulose when nitrated so as to produce a more fluid and less viscous solution, will, upon evaporation, produce a more difficultly permeable film than the same weight of viscous pyroxylin

According to A. Schoep[1] it is incorrect to compare the action of a filter with that of a fine sieve; owing to electrical phenomena, adhesion and adsorption by the filter of the substance in suspension, particles much smaller than the pores of the filter may be retained by the latter. In filtration through collodion membranes, and in the "ultrafiltration" of H. Bechhold,[2] and of E. Hatschek,[3] a certain pressure—from 0.2-10 atms.—is required. The author has succeeded in preparing membranes by means of which he has (1) filtered a colloidal solution of iron hydroxide, (2) separated a mixture of Prussian blue and hemaglobin in aqueous solution, and (3) separated colloidal arsenic sulfide, and (4) obtained a perfectly clear serum from the filtration of milk, without the use of external pressure. The membranes are composed of collodion, modified by the addition of castor oil and glycerol to the nitrocellulose solution. By varying the proportion of the components, membranes of any desired degree of permeability may be prepared.

In the formation of collodion filters as above described, A. Schoep[4] has found the following proportion of ingredients to give the best results: (1) Pyroxylin, 4; castor oil, 3.5; and ether-alcohol, 92.5 parts; and (2) Pyroxylin, 4; castor oil, 4, and ether-alcohol, 92 parts. The solvent consisted of 10 parts of alcohol, and 80 parts of ether. By adding to either of these elastic colloids

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dissolved in the same menstruum. (2) The same pyroxylin will vary in porosity depending only upon the solvent in which it has been dissolved, an amyl acetate solution of a cellulose nitrate, yielding a more compact and difficultly dialyzable film, than the same pyroxylin dissolved in ether-alcohol. The introduction of minute quantities of vegetable or animal oils, Canada balsam, turpentine or other water-repellent bodies in a collodion solution will materially affect the speed of osmosis through the film when evaporated to dryness. It is suggested that the lack of concordance of results in this field may, in no small measure, be attributable to insufficient appreciation of the value of these two facts.

[1] Bull. Soc. Chim. Belg. 1910, **24**, 278, abst. J. S. C. I. 1910, **29**, 1041; C. A. 1911, **5**, 1240, 2350; J. C. S. 1910, **98**, ii, 1049; Chem. Zentr. 1910, **81**, II, 1794; 1911, **82**, I, 1021.

[2] Zts. Chem. und Ind. der Kolloide, 1906, **1**, 107, Biochem. Zts. 1907, **6**, 379; Elektrochem. 1907, **13**, 527; abst. C. A. 1907, **1**, 2762; 1908, **2**, 1155, 1225, 3183; J. C. S. 1908, **94**, ii, 24, 823; J. S. C. I. 1907, **26**, 993; Bull. Soc. Chim. 1908, **4**, 1032; Chem. Zentr. 1907, **78**, II, 1374; 1908, **79**, I, 193; Jahr. Chem. 1905-8, I, 264, 265, 267; Zts. physik. Chem. 1907; **60**, 257; 1908, **64**, 328.

[3] J. S. C. I. 1910, **29**, 125; abst. C. A. 1910, **4**, 1121; Chem. Zentr. 1910, **81**, I, 1181, 2136; Jahr. Chem. 1910, **63**, I, 130; Zts. ang. Chem. 1910, **23**, 1912.

[4] Bull. Soc. Chim. Belg. 1910, **24**, 354; abst. J. S. C. I. 1910, **29**, 1289; Chem. Zentr. 1910, **81**, II, 1794; 1911, **82**, I, 1021.

variable quantities of glycerol, mixtures were obtained, which after the evaporation of the solvent, left membranes through which certain colloidal emulsions and solutions could be filtered without the use of external pressure, the rate of filtration being 600 cc. per hour with a height of liquid in the filter membrane of 27 centimeters. It was proven that there was no adsorption of colloidal bodies by the substance of the membrane during filtration.

H. de Mosenthal[1] determined that cellulose nitrate in acetone solution is dialyzable through both animal and vegetable membranes, acetone being used as the external liquid. In fractional dialysis, examination of the fractions have shown them to be identical in nitrogen content with the substance originally dissolved.

According to J. Malfitano,[2] a suitable apparatus for filtering under pressure through collodion membranes results when the membrane is formed upon a network or groundwork of thick threads or filaments of the same material. The threads are formed by squirting the collodion through a fine orifice, and then drying. The thread may be wound spirally on a glass cylinder, or deposited in a network pattern on a glass plate or other smooth surface. A flexible border is then formed by means of liquid collodion, as described in the main patent.

F. Grenet and Salimbeni[3] have succeeded in preparing a collodion filter for general use, their method being to dip an ordinary Chamberland candle into a solution of a collodion containing 10% glycerol, the latter preventing the collodion drying and thus becoming useless. Before doing so, it is necessary to remove all the air from the candle by plunging it in water, or better in alcohol. Such a filter is said to prevent the passage of ultramicroscopic organisms, and to retain its efficiency for at least a year. To prevent the growth of moulds upon it, it is advizable to add a trace of formaldehyde to the collodion solution.

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[1] J. S. C. I. 1907, **26**, 443; abst. C. A. 1907, **1**, 1770; Zts. ang. Chem. 1907, **20**, 1970; Jahr. Chem. 1905–08, II, 975; J. Soc. Dyers Color, 1907, **23**, 214; Chem. News, 1907, **95**, 189; Chem. Zentr. 1907, **78**, II, 687, 2039; 1911, **82**, II, 1120.

[2] E. P. 8545, 1910; F. P. 401926; Add. May 4, 1911; abst. J. S. C. I. 1910, **29**, 1289; 1911, **30**, 1300.

[3] J. Roy. Micr. Soc. 1911, 543; Compt. rend. 1911, **152**, 916; abst. C. A. 1912, **6**, 3139; Chem. Zentr. 1911, **82**, I, 1603; Chem. Ztg. 1911, **35**, 452.

Collapsible tubes and other hollow articles are made according to the L. Feval process,[1] by dipping a non-collapsible form into a pyroxylin composition, drying the coating picked up by the former by subjecting it to the action of boiling water or steam, and finally eliminating the last traces of solvent by boiling the product in water or otherwise heating it.

In the investigation of ultra-filtration and pressure dialysis, cylindrical bags of collodion are made by G. Walpole,[2] by pouring an alcohol-ether collodion solution into test-tubes. After evaporation of the solvent, the tube is immersed in water for a time, and then the collodion lining can be easily removed; it should be stored under water. Such membranes can be used for the filtration of tetanus and diphtheria toxins, but they lack uniformity and do not withstand pressures above 2 atm. Flat membranes can be made with remarkable uniformity by pouring the collodion solution on to a leveled glass plate, and removing the film under water. Films made to a standard pattern were found to retain quantitatively all the antigens experimented with; they filtered rapidly and were highly permeable to salts and water. They may be used in the construction of a continuous apparatus, e. g., a filter press for the filtration and pressure dialysis of toxins.

In the detection and concentration of antigens, with especial reference to the study of diphtheria and tetanus toxins, A. Glenny and G. Walpole[3] have found, that as antigens do not traverse collodion-water membranes these can be used for the routine purification and concentration of toxins, and also for the preliminary examination of the specificity or otherwise of the toxic constituents of any cultural fluid. The purification and concentration of diphtheria toxin is performed by means of dialysis under pressure, acidifying, centrifuging, and re-dissolving the precipitate in a trace of alkali. With these membranes, mallein and tuberculin were readily separated from glycerol and adherent

[1] U. S. P. 706541, 1902; abst. J. S. C. I. 1902, **21**, 1151.

[2] Biochem. J. 1915, **9**, 284; abst. J. S. C. I. 1915, **34**, 819; abst. C. A. 1915, **9**, 3253; 1916, **10**, 3082; J. C. S. 1915, **108**, ii, 549; J. S. C. I. 1915, **34**, 819; Chem. Zentr. 1916, **87**, II, 1173.

[3] Biochem. J. 1915, **9**, 298; abst. J. S. C. I. 1915, **34**, 816; abst. C. A. 1915, **9**, 3262; J. C. S. 1915, **108**, i, 750; Chem. Zentr. 1916, **87**, II, 1174.

nitrogenous matter, and tetanus toxin was purified by ultrafiltration followed by pressure dialysis.

In the preparation of collodion dialyzers of graded permeability according to the method of W. Brown,[1] air-dried collodion membranes are treated with varying percentages of alcohol in water for a suitable length of time, and then washed with water. The permeability of such membranes is directly related to the strength of the alcohol employed, so that, by the use of various concentrations, membranes of almost any degree of permeability may be obtained, e. g., from those which will keep back copper sulfate to those which are permeable to such a highly colloidal substance as aniline blue.

The C. Farmer process for the preparation of uniform collodion membranes for dialysis,[2] involves the formation of the membrane by filling a glass tube with collodion solution (3 gm. of dried guncotton to 50 cc. of a mixture of equal parts of absolute alcohol and ether), inverting, and allowing to drain for one minute. The tube is then dried for one minute in a current of air and afterwards filled with cold water. After a few minutes, the thin membrane can be removed from the walls of the glass tube with the aid of a pair of forceps. The permeability of the membrane may be changed by varying the period of drying. Convenient apparatus for performing these operations is described in detail.

J. Loeb[3] has studied the influence of electrolytes on the electrification and the rate of diffusion of water through collodion membranes, and has found that when pure water is separated by a collodion membrane from an aqueous solution of an electrolyte, the rate of diffusion of water is influenced not only by the forces of gas pressure, but also by electrical forces. The electric attraction of water caused by the electrolyte augments with increasing concentration of the electrolyte, more rapidly at low concentrations than at high. It is tentatively assumed that the electrolyte, collodion and water are arranged in the collodion membrane in a definite pattern held together by chemical forces, but with the molecules of water and the cations retaining their mobility in liquids. The rate of diffusion of an electrolyte through a collodion membrane from solution to pure solvent seems to largely obey the kinetic theory, in that it is approximately proportional to the concentration of the electrolyte, and is the same for equal concentrations of LiCl, NaCl, $MgCl_2$ and $CaCl_2$.

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[1] Biochem. J. 1915, **9**, 320, 591; abst. J. S. C. I. 1915, **34**, 1118; C. A. 1916, **10**, 1360; J. C. S. 1915, **108**, ii, 824; Chem. Zentr. 1916, **87**, II, 1102, 1174.

[2] J. Biol. Chem. 1917, **32**, 447; J. C. S. 1918, **114**, ii, 63; J. S. C. I. 1918, **37**, 108-A; C. A. 1918, **12**, 376.

[3] J. Gen. Physiol. 1919, **1**, 717; abst. C. A. 1919, **13**, 2041.

In investigating the influence of a slight modification of the collodion membrane on the sign of the electrification of water,[1] it was found that collodion membranes which have been treated with 1% gelatin solutions show a different osmotic behavior than the untreated membranes, manifested only towards solutions of electrolytes (i. e., acids, acid salts, salts with tervalent and quadrivalent cations), which tend to induce negative electrification of the water particles diffusing through the membranes; towards solutions of salts and alkalis which induce positive electrification. With untreated membranes, no water diffuses into the solutions. Collodion membranes treated with casein, egg albumin, blood albumin or edestin behave like gelatin treated membranes, but treatment with peptone prepared from egg albumin, alanine, or starch has no effect. In treating the collodion bags with gelatin, the gelatin solution was allowed to remain over night, then removed when the bag was washed six or more times with warm water. The bag was then allowed to remain in water for days to remove the last traces of gelatin. The effects of gelatin treatment are retained by the bags for a long time, even with continued use.

In a later communication[2] on the influence of the concentration of electrolytes on some physical properties of colloids and crystalloids, 1% solutions of metal gelatinate (sodium gelatinate) were separated from water by collodion membranes, and the rate of diffusion on water into the gelatinate solution, measured by the rise of the liquid in a manometer. In all cases, it was found that water diffuses through collodion membranes in the form of positively charged particles.

The differentiation of the Eberth Coli group of bacterial organisms may, according to A. Hollande and J. Beauverie,[1] be accomplished by means of collodion test papers, using for this purpose papers dipped in silver nitrate, glucose-neutral red, lead acetate, and litmus-orcein-lactose, which, after drying, are plunged into a mixture of alcohol and ether containing 10% of nitrocellulose.

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[1] J. Loeb, J. Gen. Physiol. 1920, **2**, 255; abst. C. A. 1920, **14**, 676. In a previous communication (J. Gen. Physiology, 1919, **2**, 200; abst. C. A. 1920, **14**, 187), solutions of non-electrolytes, sucrose, glucose, glycerol, separated from pure water by a collodion membrane, were found to influence the initial rate of diffusion of water through the membrane approximately in proportion to their concentrations.

[2] J. Loeb, J. Gen. Physiol. 1920, **2**, 273; abst. C. A. 1920, **14**, 676.

J. Duclaux and A. Hamelin[2] have recorded some observations on the use of collodion filters, in which they find the usual difficulty in their employment is that they cannot be dried or sterilized by heat. These authors have succeeded in preparing collodion filters which obviate these difficulties, but the results are not sufficiently constant to be satisfactory. They, therefore, advocate the use of cellulose filters prepared by mixing cellulose with Schweizer's solution, or by denitrating nitrocellulose with ammonium hydrosulfide. Filters prepared in this manner, it is stated, may be dried any number of times, or placed in boiling water without being affected. They also resist the action of alcohol, ether or acetone. In filtering liquids containing very fine particles, the process is slow. It is impossible to apply air pressure, lest the cellulose ruptures, the idea being especially recommended in determining osmotic pressure as an accelerating agent. To this end the authors employ a solution of Congo Red, which does not penetrate the cellulose filter, but exerts a considerable amount of osmotic pressure upon it. By this means they were able to increase the rapidity of filtration by as much as seven times without endangering the filter.

The employment of collodion membranes in physical experiments is becoming of increasing importance and usefulness.

Reduction of Inflammability. The subject of diminution in inflammability of the nitrocelluloses is intimately associated with *stability*, many of the generalizations brought forth in that topic holding good in this connection. Broadly speaking, those products added to nitrocellulose to increase the stability are relatively non-inflammable, and hence the converse is also true, that reducing the inflammability by the addition of foreign bodies usually tends to increase the stability. However, there is this important difference between the two, while stabilizers are usually added in relatively small amounts—generally in amounts under 1% based on the weight of the cellulose ester—inflammability diminishing materials (non-inflammable compounds) are usually introduced in many times that amount in order to reduce the flammability to the desired degree. There is a distinction, but not a differentiation. Whereas stabilizers are usually ant-acids, "non-inflammabilizers" are often of acid reaction, but are added in such large amounts, that the speed of burning is reduced to a point where the development of a slight acidity is not detrimental, or at least is not dangerous. Stabilizers are usually soluble in the nitrocellulose menstrua and hence do not affect the appearance of the finished product, especially the transparency. Conversely inasmuch as inorganic salts or oxides are often employed to diminish inflammability,. the translucency and opacity are increased in proportion to the amount of material added.

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[1] Compt. rend. Soc. Biol. 1915, **78**, 722; J. Roy. Micr. Soc. 1916, 241.

[2] Ann. Inst. Pasteur, 1911, **25**, 145; abst. J. Roy. Micr. Soc. 1911, 548.

It was early recognized that the cellulose nitrates possess the property of being readily gelatinized by means of direct, ancillary or latent solvents and solvent combinations, and are, therefore, susceptible of being worked into a variety of forms, as rods, tubes and sheets. The subject of inflammability in connection with nitrocotton combinations, is of especial importance in conjunction with artificial filaments and solid nitrocellulose combinations analogous to celluloid. With the former, the inflammability is reduced by actual decomposition of the cellulose ester aggregate by the withdrawal of the nitrogen in the process of denitration (see pp. 1898–1900). In this operation, however, the ester is decomposed by the elimination of the nitric groups and a modified cellulose results, containing but a few tenths of 1% of nitrogen, and the product thus formed is insoluble in all cellulose ester solvents, having lost the valuable technical property of thermoplasticity.

While the pyroxylin plastics are inflammable, they are not explosive, their heat of decomposition fluctuating within wide limits due to variations in methods of manufacture, the efficiency of the stabilizing agents introduced, and the amount and nature of the pigment portion which they contain. Those pigments, as zinc oxide and metallic carbonates increase the stability and diminish the speed of burning by virtue of their incombustible inorganic mass, and the alkalinity of the base acting as a neutralizant for the comparatively small amounts of acid slowly liberated.

Notwithstanding the plastifying agents which are added to the nitrocellulose in the formation of bodies analogous to the celluloids, they partake essentially of the properties of the cellulose nitrates, and hence are capable of ignition and spontaneous decomposition. Their manufacture, therefore, contain elements of danger, and their storage and transportation is attended with certain risks. Furthermore, in the "moving picture" industry, which has developed with a rapidity little dreamed of a few years ago, the safeguards which have been thrown around it by municipal and governmental legislation as the result of disastrous accidents from ignition of picture films, have only heightened the interest in the problem of reducing the inflammability of the nitric esters to the maximum of safety compatible with the preservation of the desirable physical and chemical properties. A cursory survey of this field will disclose how the question of the attenuation of inflammability has been approached from almost every conceivable angle, and it must be said, with considerable success.

When denitration of the pyroxylin was so successfully applied in connection with artificial filaments, it was considered but a single step in advancement to adapt it to moldable nitrocelluloses, but it was immediately found that denitrated cellulose nitrate and camphor did not produce a moldable product in any sense of the word, and the idea was abandoned.

The methods, therefore, which have been proposed and which contain an element of permanency, may be subdivided into two groups:

1. Those which are applicable to cellulose esters which do not diminish the transparency of the product, i. e., in which the added ingredient does not affect the original appearance of the nitrocotton. In this class, pigments and lakes are, of course, precluded.

2. Those in which the reduction in inflammability is due to colored matter in solution, or solids in suspension, and in which, therefore, the finished product is either translucent or opaque.

Those of the first group in general, comprize inorganic salts soluble in alcohol, whereby they may be introduced into the pyroxylin mixture by means of a solvent combination agreeable to both, i. e., alcohol. Many of the halogen compounds of calcium, magnesium, manganese and aluminium are comprehended in this classification. Their great drawback is a well marked deliquescence, and the fact that, being water-soluble, pyroxylin combinations containing these salts are effected by moisture, and are usually waterproofed by the superficial application of a pyroxylin lacquer. The chlorides, less so the bromides and iodides, of mercuric, cupric, cadmium, aluminium, ferric iron, chromium, nickel, manganese, zinc, cobalt, lithium, ammonium and strontium have been advocated for this purpose, but many of them are inadmissable on account of deficient solubility in alcohol.

M. Asselot[1] adds an alcoholic solution of magnesium chloride to the celluloid or nitrocellulose dissolved in acetone. W. Parkin[2] employs a mixture of aluminium, strontium and magnesium chlorides in methyl alcohol. D. Bachrach advocated alcoholic calcium chloride,[3] while calcium bromide, sulfate or oxalate, formed the essence of the invention of A. Mabille and G. Leclerc,[4] the latter two salts being insoluble. The manganous chloride of P. Marino,[5] the zinc chloride and oxide combination of C. Clauss,[6]

[1] E. P. 6389, 1896; abst. J S. C. I 1896, **15,** 313; 1897, **16,** 84, 151. D. R. P 93797, 1906; abst. Wag. Jahr. 1897, **43,** 1103, Chem. Centr. 1897, **68,** II, 927. F. P. 255002, Phot. Times, 1897, 248. For general articles on uninflammable celluloid see Hildebrand, Zts Bursten, 1908, **27,** 594; Gewerbebl. Wurt. 1897, **49,** 373; Amer. Apoth Ztg. 1898, **18,** 129. Stubling, Celluloid, 1907, **7,** 99, Net. Arb. 1888, **14,** 753

[2] F. P. 344501, 347446, 1904, abst. Mon Sci 1906, **65,** 47, 49; J. S. C. I. 1904, **23,** 1111. D. R. P. 171694, 1904, abst Chem. Centr. 1906, **77,** II, 736; Jahr. Chem. 1905-1908, II, 992, Zts ang Chem. 1906, **19,** 244. See also E. P. 6389, 1896. F. P. 347443. W. Parkin and A. Williams, E. P. 26657, 1909; abst. J. S. C I. 1910, **29,** 1152. F. P. 421010. Proc. Amer. Pharm. Assoc. 1906, **54,** 909; Pharm Ztg. 1906, 227 W. Parkin, A Williams and T. Casson, E. P. 28212, 1903, F. P. 344501, abst. J. S. C. I. 1904, **23,** 1111, 1159.

[3] U. S. P. 667759, 1901; abst. J A. C. S. 1902, **24,** 56. U. S. P. 743422, 1903; abst. Mon Sci. 1904, **61,** 86; Chem. Zts. 1904, **3,** 244. E. P. 22970, 1903; abst. J. S. C. I. 1903, **22,** 75; Chem. Ztg. 1905, **29,** 225. F. P. 337060, 1903; abst. Mon. Sci. 1905, **63,** 85. Belg. P. 15462.

[4] F. P. 317844, 1902; abst. Mon. Sci. 1903, **59,** 120; 1908, **69,** 655.

[5] U. S. P. 893634, 1908; abst. Mon. Sci. 1910, **73,** 96; C. A. 1908, **2,** 2874. D. R. P. 206471; abst. Chem. Zentr. 1909, **80,** I, 1064; Chem. Ztg. Rep. 1909, **33,** 91; Zts. ang. Chem. 1909, **22,** 504; Jahr. Chem. 1909, **62,** II, 390; Chem. Zts. 1909, **8,** No. 1279. E. P. 5891, 1907; abst. J. S. C. I. 1907, **26,** 1107. F. P. 376399, 1907. Swiss P. 42529, 1907. Belg. P. 203274, 1907. Can. P. 109778, 1908. Dan. P. 10937, 1908. E. P. 7430, 1908; abst. C. A. 1909, **3,** 2628; J. S. C. I. 1909, **28,** 812. Swiss P. 48281. F. P. 401527, 1909; abst. J. S. C. I. 1909, **28,** 1163; Mon. Sci. 1910, **73,** 292, 296; 1911, **75,** 153.

Marino has protected by patent application the use of the following for the reduction of inflammability in connection with nitrocellulose: aluminium hydroxide and iodide; barium, calcium, iron (ferrous and ferric), lead, the aluminium chloride and sulfate mixture of P. Prost and E. Michey,[1] the stannous chloride and colophony as advized by S. Assadas,[2] and the mixed halides of the Westfälisch Anhaltische Sprengstoffe A. G.,[3] indicate the salts which apparently have found most favor. A. Schwarcman[4] proposes to directly chlorinate the pyroxylin with nascent chlorine, but it is difficult to see wherein a useful product is produced by following out the suggestions as embodied in his patent. All the above alcohol soluble halides give transparent products.

The general method of incorporation is to dissolve the salts alone or together in a small bulk of alcohol, filter off any undissolved residue, and then mix this solution in the desired proportion with an acetone or other low boiling solvent in which the nitrocellulose or celluloid has been softened or dissolved. Excess of solvent is then removed in any convenient manner, and the finished product results. H. Beau[5] adds an approximately 20% solution of $CaCl_2$ in acetone, to a thick celluloid mixture, so that the finished product contains one part of metallic salt to 10 of celluloid, and the mass masticated on hot rolls until the desired amount of solvent has been removed. It will be remembered that an alcoholic solution of calcium chloride is an energetic

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magnesium chromates, and phosphates; calcium arsenite and arsenate, cobalt phosphate, lead fluoride and nitrite, chromium oxide, carbon tetrachloride and trichlornitromethane.

6. E. P. 3072, 1881; abst. Chem. Ind. 1881, **4**, 280; J. S. C. I. 1882, **1**, 201. D. R. P. 17026, 1881; abst. Dingl. Poly. 1882, **243**, 434; Wag. Jahr. 1881, **52**, 949.

1. F. P. 351555, 1905; abst. Mon. Sci. 1906, **65**, 49; Chem. Zts. 1905, **4**, 333. Addition 4602 to F. P. 351555; abst. J. S. C. I. 1905, **24**, 855. F. P. 421854. Belg. P. 181151. E. P. 5130, 1905.

2. S. Assadas, E. P. 9982, 1908; abst. J. S. C. I. 1909, **28**, 671. F. P. 387537, 1907; abst. J. S. C. I. 1908, **27**, 873; C. A. 1909, **3**, 1819; Mon. Sci. 1909, **71**, 14, adding to 1 k. pyroxylin, colophony (25–200 gm.), stannous chloride (200–400 gm.), ammonium chloride (5–50 gm.), and carbon tetrachloride (5–50 gm.). "Metallodion," formed by mixing oxides or salts (lead peroxide), carbon and nitrocellulose; and "metallodium," consisting of amidocellulose salts and carbon, are uninflammable combinations of H. Aron, E. P. 2943, 1882; 21957, 1882.

3. E. P. 26617, 1901; abst. Arms Expl. 1903, **11**, 17; J. S. C. I. 1902, **21**, 1471. E. P. 3334, 1902; abst. J. S. C. I. 1903, **22**, 229; J. Soc. Dyers Color. 1904, **20**, 63. E. P. 13531, 1903; abst. Arms Expl. 1904, **12**, 82; J. S. C. I. 1904, **23**, 560. Second add. June 18, 1903, to F. P. 316569, 1901; abst. J. S. C. I. 1903, **22**, 561, 1308; Chem. Zts. 1904, **3**, 116.

4. U. S. P. 1323792, 1919; abst. C. A. 1920, **13**, 346; J. S. C. I. 1920, **39**, 60-A.

5. F. P. 322457, 1902; abst. Mon. Sci. 1903, **59**, 127; J. S. C. I. 1903, **22**, 377.

solvent of the cellulose nitrates, even in the cold.

Blanchin[1] has proposed to add calcium chloride with about half its weight of manganous chloride to nitrocellulose dissolved in a suitable solvent, the total amount of metallic salts to be added being up to 40% of the weight of the cellulose ester. The brilliancy and appearance of the finished product is said to be enhanced by the addition of small amounts of carbon tetrachloride. To the finished substance the name Pyrosa has been given.

Gunnot, Firetard and Herward[2] combine zinc and stannous chlorides in amyl acetate. W. Stevens[3] proposes to make uninflammable plastic of pyroxylin gelatinized with amyl acetate, to which has been added zinc chloride and camphor, and to which a small amount of sodium carbonate has been incorporated. An alternate method is to mix nitrocellulose (150 parts), zinc chloride (100 parts), camphor (60 parts), sodium carbonate (15 parts), with amyl acetate and methylated spirits, the mass being incorporated in a suitable machine arranged to minimize evaporation. A. Petit[4] used 7 parts of gum solution, and 5 parts of stannous chloride dissolved in benzene, to each 100 parts of nitrocellulose.

L. Béthisy[5] decreases the inflammability of pyroxylin combinations by the use of zinc chloride in ether, together with gelatin and vaseline. J. Nigro and P. Hollande[6] add 1 part of powdered $MgCl_2$ in 3 parts of alcohol to a solution of 1 part of celluloid or nitrocellulose in 10 parts of acetone. There is obtained after thorough mixing and drying a relatively non-inflammable product, the transparency and elasticity of which, according to the patentees, compare favorably with that of celluloid.

One of the earliest processes for rendering nitrocellulose and celluloid non-inflammable is due to C. Stocker,[1] and "Stocker's unburnable collodion" was heralded far and wide as the successful solution of the problem. In this method, 100 parts nitrocellulose is mixed with camphor (400), stannous chloride 70, and alcohol 100, and after standing for 12 hours for the ingredients to become thoroughly intermingled, the mass is led through heated rollers, and worked until a homogeneous, transparent product results. The claim is made for this product that it will only burn when placed directly in a flame, and after the removal of the flame, continues to glow only. The addition of other salts such as the chlorides of nickel, copper, cobalt and manganese are also suggested to both color the product and further reduce the inflammability.

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[1] F. P. 364690, 1906; abst. C. A. 1907, **1**, 2959; J. S. C. I. 1906, **25**, 951; Mon. Sci. 1907, **67**, 125; Chem. Zts. 1906, **5**, 399.

[2] Belg. P. 229253, 1910.

[3] E. P. 4390, 1908; abst. J. S. C. I. 1909, **28**, 381; C. A. 1909, **3**, 2381. J. Stevens, U. S. P. 612066, 1898.

[4] U. S. P. 662961, 1900; abst. Mon. Sci. 1901, **57**, 127. E. P. 22867, 1899; abst. J. S. C. I. 1900, **19**, 461. F. P. 294379, 1899; abst. Rev. Chim. 1900, **2**, 260.

[5] D. R. P. 110012, 1901; abst. Chem. Ztg. 1900, **24**, 473; Jahr. Chem. 1900, **53**, 850. U. S. P. 894108, 1908; abst. Mon. Sci. 1910, **73**, 95; C. A. 1908, **2**, 2874. F. P. 368004, 1906; abst. J. S. C. I. 1906, **25**, 1231; Mon. Sci. 1908, **69**, 142; C. A. 1909, **3**, 251. See also E. P. 11927, 1898; abst. J. S. C. I. 1899, **18**, 602.

[6] F. P. 420212, 1910; abst. J. S. C. I. 1911, **30**, 353; Mon. Sci. 1913, **79**, 30.

P. Prost, E. Michey and Cochalat[2] protect an uninflammable material called by them "Prostine," made by mixing certain chlorides or salts of aluminium with nitrocellulose. B. Buchstab[3] works up pyroxylin with stannous chloride and lactic acid, but the latter is water soluble and hygroscopic, and must be protected from moisture by a superficial coating of nitrocotton.

All the alcoholic soluble salts mentioned above possess the disadvantage that they are also soluble in water, the finished product containing such salts being impaired if subjected to the atmosphere (moisture). Disadvantages of deliquescent salts used in this connection are the possible formation of a film of moisture on the surface of the cellulose ester composition, and this also may assist in the volatilization of such products as camphor which may be a constituent. The addition of bodies causing double decomposition of the deliquescent, alcohol-soluble inorganic salt usually interferes with the transparency in overcoming the above objections, i. e., the addition of soluble sulfates to calcium chloride, resulting in the precipitation of the non-deliquescent, water-insoluble calcium sulfate, which, however, renders

[1] E. P. 16330, 1887; D. R. P. 45024, 1888; abst. Ber. 1888, **21**, 913; Chem. Tech. Rep. 1888, **27**, II, 125; Chem. Tech. Jahr. 1888, **11**, 182; Wag. Jahr. 1888, **34**, 1163; Indbl. 1889, 39.

[2] Belg. P. 176057, 1904. P. Prost and E. Michey, F. P. 351555, first add. dated March 18, 1905; abst. J. S. C. I. 1905, **24**, 855, 984; Mon. Sci. 1906, **65**, 49; Chem. Zts. 1905, **4**, 303.

[3] F. P. 408406, 1908; abst. J. S. C. I. 1910, **29**, 557; Mon. Sci. 1910, **73**, 300. D. R. P. 214398, 1909; abst. J. S. C. I. 1909, **28**, 1221; Mon. Sci. 1913, **79**, 38; Chem. Zentr. 1909, **80**, II, 1515; Chem. Tech. Rep. 1909, **33**, 564; Chem. Zts. 1910, **9**, 1862; Wag. Jahr. 1909, **55**, II, 555; Zts. ang. Chem. 1910, **23**, 384.

the pyroxylin opaque in proportion to the $CaSO_4$ present.

In addition to the class of inorganic halogens which have been mentioned above, are a number of products which possess the combined properties of stability as well as reduction of inflammability. For instance, the Societe Industrielle de Celluloid[1] incorporate a maltodextrin together with a small amount of borax, their preferred combination being to admix 60 parts nitrocellulose, alcohol containing camphor 60 parts, maltodextrin 18 parts, and about 5% of borax The solvents are removed by mastication and rolling.

F. Matthews and H. Elder[2] react by sulfur dioxide on the unsaturated hydrocarbons *pseudo*butylene, amylene and ethylene, which are polymerized by exposure to ultra-violet light, and are then admixed with pyroxylin by means of a solvent suitable to both, such as acetone. L. Labbe[3] adds gelatin and magnesium acetate; F. Gaens[4] mixes the nitrocotton with humate of ammonia; J. Ducruet[5] depends upon carbon tetrachloride for diminishing combustibility, which is also the essence of the process of C. Ellis.[6]

L. Béthisy, L. Fouchard and E. Vignes[7] have received patent protection for the use of ammonium sulfocyanide and *Unona selanica* in this connection. All the ammonium compounds are, of course, active deterrents of combustion, but this particular one is unusually soluble in water and deliquescent, and compared with other equally efficient and more readily available ammonium compounds, is unduly expensive. The phenol-aldehydes have been put forward by H. Matheson[8] of E. du Pont de Nemours

[1] F. P. 407846, 1909; abst. J. S. C. I. 1910, **29**, 622; Mon. Sci. 1912, **77**, 6 D. R. P. 221081, 1909; abst. C. A. 1910, **4**, 2732; Mon. Sci. 1914, **81**, 133; Chem Zentr. 1910, **80**, I, 1663; Chem. Ztg. Rep. 1910, **34**, 220; Jahr. Chem 1910, **63**, II, 429.

[2] E. P. 11635, 1914; abst. J S. C. I 1915, **34**, 670; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 192; C. A. 1915, **9**, 2971.

[3] F. P. 410973, 1909; abst. Mon. Sci. 1912, **77**, 7.

[4] D. R. P. 48933, 1889; abst. Ber. 1889, **22**, 525; Chem. Centr. 1890, **61**, I, 560; Tech. Chem. Jahr. 1889, **12**, 163; Jahr. Chem. 1889, **42**, 2682; Wag. Jahr. 1889, **35**, 473; Chem. Ind. 1889, **12**, 466; Zts. ang. Chem. 1889, **2**, 554; Chem. Tech. Rep. 1889, **18**, II, 171.

[5] F. P. 341158, 1904; abst Mon. Sci 1906, **65**, 47; J. S. C. I. 1904, **23**, 885. See also G. Dilette and J. Talabot, F. P. 341927, 1904; abst. Mon. Sci. 1905, **63**, 150; Chem. Zts. 1904, **3**, 602.

[6] F. P. 363506, 1906; abst. C. A. 1907, **1**, 2325; Mon. Sci. 1907, **67**, 92.

[7] F. P. 368004, 1906; abst. C. A. 1909, **3**, 251; Mon. Sci. 1908, **69**, 142; Chem. Ztg. Rep. 1906, **30**, 426. Motography, Aug. 12, 1912, 36.

[8] U. S. P. 1309581, 1919; abst. C. A. 1919, **13**, 2278; J. S. C. I. 1919, **38**, 678-A.

& Co., in which he has proposed to render a surface having a nitrocellulose coating fire-resistant by the application thereto and thereon, of a condensation product of phenol and formaldehyde. On account of the non-pliability of these condensation products, their use in this connection would be limited to rigid nitrocellulose articles.

C. Waller[1] both stabilizes, plasticizes and reduces the inflammability by the addition of *mono*nitronaphthalene accompanied by a small amount of paraffin and calcium carbonate, his process being designed especially for combination with the nitrostarches. The Berlin Aniline Co.[2] have protected the use of epichlorhydrin and dichlorhydrin for this purpose, while E. Callenberg[3] has advocated turpentine, and E. Steele, C. Bower and H. Poehlman[4] use nitro-phthalic acid for stabilizing and diminishing the burning capacity of their nitrocellulose explosive called "Steelite."

Dinitro-dialkyloxamides,[5] as dinitrodimethyloxamid and dinitrodiethyloxamid; soaps, as resin soap;[6] fish glue,[7] shellac,[8] sodium oleate, palmitate or stearate,[1] magnesium oleate (called in the trade, Antibenzinepyrin), and zinc acetate,[2] indicate the nature of the materials which have been proposed from time to time for this purpose.

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[1] U. S. P. 1305846, 1919; abst. C. A. 1919, **13**, 2130. Hexachlornaphthalene has been proposed by K. McElroy and C. Ellis, U. S. P. 914300, 1909; abst. C. A. 1909, **3**, 1447. See also C. Trocquenet, F. P. 362989, 1906; abst. Mon. Sci. 1907, **67**, 123; 1908, **68**, 656; 1910, **72**, 453; Chem. Zts. 1906, **5**, 303; C. A. 1907, **1**, 2956; J. S. C. I. 1906, **25**, 825, 950; E. P. 8167, 1906; abst. J. S. C. I. 1906, **25**, 950; C. A. 1907, **1**, 640, 659. H. Manissadjian, E. P. 27201, 1908; F. P. 397429, 1908; abst. J. S. C. I. 1909, **28**, 1812; C. A. 1911, **5**, 197; Mon. Sci. 1913, **78**, 392, 551.

[2] E. P. 17953, 1913; abst. J. S. C. I. 1914, **33**, 838. Belg. P. 259073, 1913; abst. Chem. Ztg. 1913, **37**, 1304. F. P. 461034, 1913; abst. Chem. Ztg. 1913, **37**, 1405; 1914, **38**, 241. Mon. Sci. 1914, **81**, 121.

[3] F. P. 288640, 1899; 322946, 1902; add. Oct. 28, 1902; abst. J. S. C. I. 1903, **22**, 380, 760; Mon. Sci. 1900, **56**, 63; Rev. Chim. Ind. 1899, **10**, 299. D. R. P. 108402, Belg. P. 145542, 1899; abst. Chem. Centr. 1900, **71**, 1150; Chem. Tech. Rep. 1900, **39**, 326; Tech. Chem. Jahr. 1899, **22**, 144; Jahr. Chem. 1900, **53**, 614; Meyer Jahr. Chem. 1900, **10**, 322; Wag. Jahr. 1900, **46**, I, 401.

[4] E. P. 14676, 1901; abst. J. S. C. I. 1902, **21**, 1155; Arms. Expl. 1902, **10**, 143.

[5] Westfälisch Anhaltische Sprengstoff A. G., D. R. P. 203190, 1907; abst. J. S. C. I. 1908, **27**, 1178; Chem. Zentr. 1908, **79**, II, 1842; Chem. Ztg. Rep. 1908, **32**, 624; Wag. Jahr. 1908, **54**, I, 437; Zts. ang. Chem. 1908, **21**, 2377; Zts. Schiess. Spreng. 1908, **3**, 417

[6] Vereinigte Köln-Rottweiler Pulverfabriken, A. G., D. R. P. 195486, 1907; abst. Chem. Zentr. 1908, **79**, I, 1236; Wag. Jahr. 1908, **54**, I, 436; J. S. C. I. 1908, **27**, 593; Zts. ang. Chem. 1908, **21**, 842; Chem. Ztg. Rep. 1908, **32**, 185; Jahr. Chem. 1905–1908, II, 981; Zts. Schiess. Spreng. 1908, **3**, 93. See also D. R. P. 175399; abst. Chem. Centr. 1906, **77**, II, 1702; Chem. Ind. 1909, **32**, 561; 1908, **31**, 206.

[7] G. Woodward, E. P. 9277, 1904; abst. J. S. C. I. 1905, **24**, 149; Chem. Ztg. Rep. 1905, **29**, 886. India P. Appl. 134, 1905. Austral. P. Appl. 2841, 1905. D. R. P. 171428, 1904; abst. Chem. Centr. 1906, **77**, II, 736; Mon. Sci. 1908, **69**, 45, 656; Jahr. Chem. 1905–1908, II, 992; Wag. Jahr.

Bodies like the paraffins, vaseline and other petroleum hydrocarbons have been extensively employed both to reduce inflammability and enhance stability, as well as their nitrated products dinitroxylene, trinitroxylene,[3] and the nitro-cumenes. The addition of paraffin,[4] beeswax,[5] cetyl palmitate and spermaceti,[6] vaseline,[7] and vegetable wax,[8] have been used in special

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1906, **52,** II, 526; Zts. ang. Chem. 1907, **20,** 368. Belg. P. 177495, 1904. U. S P. 803592, 1905; abst. Mon. Sci. 1906, **65,** 93; J. S. C. I. 1905, **24,** 1222. F. P. 344048, 1904; abst. Mon. Sci. 1906, **65,** 47; Chem. Zts. 1904, **3,** 764; J. S C. I. 1905, **24,** 1251. Aust. P. 23151; abst. J. S. C. I. 1904, **23,** 1111; Sci Amer., Feb. 17, 1906.

8. Burton, F. P. 192819, 1888; abst. Mon. Sci. 1889, **34,** 633.

1. E. P. 791, 1907; abst. C. A. 1907, **1,** 2506. Cf. E. P. 24782, 1904; abst. Meyer Jahr. Chem. 1905, **15,** 359; J. S. C. I. 1905, **24,** 105.

2. A. Wolkersdorfer, D. R P. 74855; abst. Jahr. Chem. 1894, **47,** 1134; Ber. 1894, **27,** 815; Wag. Jahr. 1894, **40,** 749; Zts. ang. Chem. 1894, **7,** 472.

3. J. Delpech, Compt. rend. 1919, **169,** 537; abst. C A. 1920, **14,** 468; J. S. C. I. 1919, **38,** 878-A; Ann. Rep. Soc. Chem. Ind. 1919, **4,** 564. Cf H de Chardonnet, Compt. rend. 1919, **167,** 581; abst. C. A. 1920, **14,** 225 For the use of naphthyl carbonate and phosphate, see E. Zühl, U. S. P. 700884, 700885, 1902; abst. Mon. Sci. 1903, **59,** 6; J. A. C. S. 1902, **24,** 520. Similar proposals to the foregoing have been advanced by M. Abelli, E. P. 21529, 1905. J. Bouchaud-Praceiq, E. P. 10129, 1908. H. Chapman, E. P. 1115, 1889. A. Combe, F. P. 438418, 1911 C. Curtis, D. Metcalf and A. Pearcy, E. P. 6756, 12404, 1898. C. Curtis and G. Andre, E. P. 5821, 1891; abst. Wag. Jahr. 1892, **38,** 377. R. Defalque, Belg. P. 189445, 1906. G. Dime, E. P. 17497, 1898; 13238, 1899. C. Duttenhofer, E. P. 19408, 1906. P. Germain, F. P. 349292, 1904; Belg. P. 180720, 1905. C. Gimonet, G. Firetard and G. Hermand, Belg. P. 229253, 1910. J. Hall, Wag. Jahr. 1874, **20,** 424; Ber. 1874, **7,** 743. W. Hodgkinson, E. P. 17456, 1888. Farbwerke vorm. Meister, Lucius & Brüning, Belg. P. 144234, 148560; E. P. 15355, 1899; Aust. P. Anm. 1713, 1900. W. Merckens and B. Manissadjian, D. R. P. Anm. M-37763, M-37495; Swiss P. 51960, 1910; Belg. P. 223996, 224741, 1910. A. Nobel, E. P. 5382, 1884. Potchy, Gewerbebl. Württemb. 1899, **51,** 61; S. Young, E. P. 11495, 1911

4. Experiments conducted by the French Commission on Explosives, Mem. poudres, 1882-1883, **1,** 483; 1884-1889, **2,** 586, 605.

5. S. Mackie and C. Faure, E. P. 1830, 1873; abst. Chem. Ind. 1878, **1,** 205. Chem. News, 1874, **29,** 166; Dingl. Poly. 1874, **213,** 174; Ber. 1874, **6,** 741; Jahr. Chem. 1874, **27,** 1123. S. Mackie, C. Faure and G. Trench, E. P. 2062, 1874; abst. Ber. 1876, **9,** 205; Bayer Ind. Gewer. 1876, 141; Wag. Jahr. 1876, **22,** 480; Chem. Tech. Rep. 1876, **15,** 388; Zts. Chem. Grossgew. 1876, **1,** 233.

6. J. Lewin, E. P. 2149, 1880. R. Sjöberg, E. P. 2302, 1881; abst. Dingl. Poly. 1882, **246,** 184; Chem. Ind. 1882, **5,** 120; Jahr. Chem. 1882, **35,** 1411; Bull. Soc. Chim. 1882, **38,** 601; Ber. 1882, **15,** 266; Wag. Jahr. 1882, **28,** 404; Chem. Tech. Rep. 1883, **22,** I, 153; Proc. U. S. Nav. Inst. 1883, **9,** 751; Chem. News, 1885, **52,** 101.

7. Muencke, D. R. P. 690, 1877; abst. Wag. Jahr. 1878, **24,** 466; Chem. Ind. 1878, **1,** 127; Zts. Chem. Grosgew. 1878, **3,** 680; Poly. Notiz.

instances, but only where specific properties were desired.[1]

J. Clarac[2] renders pyroxylin-containing products uninflammable by incorporating with them "resinates" or "resinoleates" made by the treatment of vegetable oils with metallic oxides. Analogous are the ideas of E. Peyrusson,[3] who prepares the ricinoleates and sulforicinoleates of magnesium, zinc, aluminium and lead, the magnesium ricinoleate being especially suitable for blending with nitrocellulose. The method of use is to incorporate the nitrocellulose by means of acetone or methyl alcohol with the respective ricinoleate in which they are readily soluble, the product formed being but slightly inflammable, translucent, firm, and unaltered on exposure to the atmosphere.

Boric acid and the water-soluble borates have long been known to possess valuable properties in reducing inflammability. W. Parkin[4] and O. Laquis, E. Pichery and A. Doucet[5] have independently described the technique of the incorporation of boric acid with nitrocellulose in which difficultly burnable compounds result in proportion to the amount of boric acid employed. The boric acid is dissolved to saturation in ethyl alcohol, and thus combined with the pyroxylin. Esters of boric acid (methyl, ethyl, propyl, butyl and amyl borates),[6] or an ether[7] solution of boric acid has also been advocated. A point recently determined[8] is that small amounts (0.2%) boric acid added to cellu-

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1878, **33**, 160; Chem. Centr. 1878, **49**, 576; Dingl. Poly. 1878, **230**, 188.

[8] L. Beals, U. S. P. 239423, 239424, 239425, 1881; abst. J. A. C. S. 1881, **3**, 68; Chem. Ind. 1881, **4**, 180.

[1] F. Quartieri and E. Molinari, E. P. 19547, 1914; abst. C. A. 1916, **10**, 694.

[2] F. P. 439648, 1911; abst. C. A. 1912, **6**, 3501; J. S. C. I. 1912, **31**, 714; Chem. Ztg. 1912, **36**, 610; Chem. Ztg. Rep. 1912, **36**, 507.

[3] F. P. 374395, 1906; abst. J. S. C. I. 1907, **26**, 776; C. A. 1909, **3**, 252. F. P. Add. 8760, 1906; abst. J. S. C. I. 1908, **27**, 765.

[4] E. P. 22381, 1904; abst. J. S. C. I. 1905, **24**, 1028; Mon. Sci. 1907, **67**, 110; 1908, **69**, 655; Chem. Ztg. 1906, **30**, 178. F. P. 347446, 1904; abst. Mon. Sci. 1906, **65**, 49; J. S. C. I. 1905, **24**, 344, 1028. D. R. P. 171428; abst. Mon. Sci. 1908, **69**, 45, 656; Chem. Centr. 1906, **77**, II, 736; Jahr. Chem. 1905–1908, II, 992; Wag. Jahr. 1906, **52**, 526; Zts. ang. Chem. 1907, **20**, 368. D. R. P. 171694, 1904; abst. Chem. Centr. 1906, **77**, II, 736; Jahr. Chem. 1905–1908, II, 992; Zts. ang. Chem. 1907, **20**, 244. Belg. P. 180098, 1904. See also W. Parkin and A. Williams, E. P. 8301, 1901; 28212, 1903; 22381, 1904; 26657, 1909; F. P. 347446, 1905; abst. J. S. C. I. 1905, **24**, 344.

[5] F. P. 345415, 1904; abst. Mon. Sci. 1906, **65**, 48; Chem. Zts. 1905, **4**, 16.

[6] F. Botrelle and G. Fretard, Belg. P. 242735, 1912.

[7] Societe Celluloid Uninflammable, Belg. P. 199328, 1907.

[8] Titanine, Ltd., and P. Bowles, E. P. 136927, 1919; abst. J. S. C. I. 1920, **39**, 164-A.

lose ester solutions tends to preserve the viscosity of the solution upon standing. "Borated benzene," which is merely a solution of boric acid in benzene, has been recently brought forward as a constituent of cellulose ester lacquers and dopes for its fire-resisting qualities.[1]

Quite similar in their action in this respect are certain compounds of silicon when combined with pyroxylin. v. Lenk long ago added water glass to "preserve" guncotton. Franke[2] patented a process of adding potassium silicate as an agglutinating material to the cellulose nitrates to decrease their burning capacity, this process being similar to that of J. Bickford and G. Smith.[3] S. de Medveczky[4] combined celluloid with water glass and then added quartz in an impalpable powder to the finished material, thus, however, producing an opaque mixture. The "apiroid" of P. Nogues and H. Proveux[5] combined silicates with aluminium acetate, whereby an aluminium silicate was formed by double decomposition, deliquescent, water-soluble potassium acetate remaining also in the plastic.

Of more valuable in this connection are members of the class of silicic esters, the so-called silicic ethers, upon which much experimentation has been done. L. Pillion[6] and E. Clement have proposed the incorporation with nitrocellulose of methyl, ethyl, propyl, butyl and amyl silicates, and certain disilicic esters[7] such as ethyl monosilicate, diethyl monosilicate, hexaethyl disilicate and diethyl disilicate, all of which are soluble in such menstrua as alcohol, ether and acetone.[8] They are added so that the proportion of silica contained therein is about 10% of the nitrocellulose present in the mixture. L. Knorr and H.

[1] D. Sutherland and Wall Paper Mgf., Ltd., E. P. 131082, 1918; abst. C. A. 1920, **14**, 131.

[2] F. P. 179452, 1886; abst. Mon. Sci. 1887, **30**, 1143.

[3] E. P. 1297, 1863.

[4] E. P. 27283, 1910; F. P. 436245, 1911; D. R. P. 239773, 1910; Belg. P. 239891, 1911; abst. C. A. 1912, **6**, 1543, 2186; J. S. C. I. 1912, **31**, 67; Chem. Zentr. 1911, **82**, II, 1501; Chem. Ind. 1911, **34**, 729; Chem. Ztg. Rep. 1911, **35**, 568; Wag. Jahr. 1911, **57**, II, 554; Zts. ang. Chem. 1911, **24**, 2288.

[5] F. P. 328054; abst. Mon. Sci. 1904, **61**, 76.

[6] D. R. P. 149764, 1902; abst. Chem. Centr. 1904, **75**, I, 1116; Chem. Ztg. 1904, **28**, 329; Wag. Jahr. 1904, **50**, II, 511; Zts. ang. Chem. 1904, **17**, 900. N. Erfind. Erfahr. 1904, **31**, 315. D. R. P. 140784.

[7] Belg. P. 225222, 1910; Span. P. 47917, 1910; F. P. 402569, 1909; E. P. 10320, 1910.

[8] F. P. 325336; abst. Mon. Sci. 1904, **61**, 44, Chem. Zts. 1903, **2**, 376.

Weyland[1] have described certain glyceryl silicates formed by the action of tetraethyl silicate upon anhydrous glycerol, being gelatin-like substances also possessing therapeutic value. *Sec-* and *ter-*glyceryl orthosilicates are alleged to be especially valuable. Their apparent valuable points are insolubility in water, non-deliquescence, and a fair degree of stability, coupled with a satisfactory solubility in those fluids which dissolve nitrocellulose.

The problem has also been approached from the viewpoint of the introduction of materials which upon heating, evolve a gas which is not a supporter of combustion, the water-soluble carbonates having been advocated for this purpose. Sodium or calcium carbonate in the hands of D. Bachrach,[2] sodium bicarbonate as perfected by G. Potts,[3] and a bicarbonate as described by P. Germain[4] are illustrative of the products employed. The liberation of ammonia, as by the use of ammonium chloride or microcosmic salt (sodium ammonium hydrogen phosphate),[5] or ammonium magnesium phosphate,[6] or magnesium borate[7] have received patent protection as being especially useful in connection with pyroxylin.

Ammonium nitrate[8] is also said to render guncotton less inflammable. M. Pollak and J. Dekoster[1] reduce inflammability by means of a tungsten salt, while organic tungsten salts[2] have also been recommended for this purpose.

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[1] U. S. P. 1178731; abst. C. A. 1916, **10**, 1577; J. S. C. I. 1916, **35**, 654. D. R. P. 285285; abst. C. A. 1916, **10**, 666; J. S. C. I. 1915, **34**, 1166; Mon. Sci. 1918, **85**, 21; Chem. Zentr. 1915, **86**, I, 373; Wag. Jahr. 1915, **61**, II, 14; Zts. ang. Chem. 1915, **28**, 373.

[2] U. S. P. 667759, 692102, 743422, 794581, Re-13793; E. P. 2339, 1901; F. P. 307743; Aust. P. 6713, 1902; abst. C. A. 1914, **8**, 3502; J. A. C. S. 1902, **24**, 56, 381; 1904, **26-R**, 273; 1906, **28-R**, 123; J. S. C. I. 1901, **20**, 741; 1902, **21**, 366; 1905, **24**, 901; 1914, **33**, 958; Mon. Sci. 1902, **58**, 77, 158; 1904, **61**, 86; Chem. Ztg. 1902, **26**, 165; 1905, **29**, 825; Chem. Zts. 1904, **3**, 244; 1905, **4**, 451; Zts. Schiess. Spreng. 1906, **1**, 50. E. P. 22970, 1903; abst. Chem. Ztg. 1905, **29**, 225; J. S. C. I. 1904, **23**, 75; Mon. Sci. 1906, **65**, 73.

[3] U. S. P. 1008615, 1911; abst. C. A. 1912, **6**, 294; J. S. C. I. 1912, **31**, 92; Mon. Sci. 1912, **77**, 159. Cf. P. Germain, F. P. 349292, 1904; abst. Mon. Sci. 1906, **65**, 49; Chem. Zts. 1905, **4**, 233; J. S. C. I. 1905, **24**, 686.

[4] F. P. 349292, 1904; abst. J. S. C. I. 1908, **27**, 686; Mon. Sci. 1906, **65**, 49; Chem. Zts. 1905, **4**, 233.

[5] E. P. 17497, 1898. See also A. Wister, U. S. P. 655845, 1900; abst. Mon. Sci. 1901, **57**, 121.

[6] J. Emhardt, U. S. P. 1329386, 1920; abst. J. S. C. I. 1920, **39**, 264-A.

[7] T. Best, E. P. 15121, 1884; abst. J. S. C. I. 1884, **3**, 586; 1885, **4**, 751; Wag. Jahr. 1885, **31**, 1149; 1886, **32**, 1004.

[8] Barbe, F. P. 159214, 1883; 168189, 1885; abst. Mon. Sci. 1884, **26**, 506; 1885, **27**, 1209. See also C. Claus, E. P. 3072, 1882; abst. J. S. C. I. 1882, **1**, 201. Equal weights of pyroxylin with zinc or lead oxychloride, the salt being finely powdered and anhydrous.

S. Hoggson and G. Pettis[3] have highly recommended the use of aluminium salts, as the alums, aluminium hydroxide in the hands of R. Plaissetty,[4] the sulfate in the experience of C. Hagemann and F. Zimmerman,[5] while aluminium acetate which is soluble in alcohol, has been used with gratifying results according to the patentees, P. Nogues and H. Proveux.[6] The method of procedure is to dissolve the salt in the minimum of alcohol, ether or acetone, and gradually add this to the nitrocellulose in solution. An amyl acetate mixture of magnesium sulfate,[7] magnesium and lead oxides,[8] or magnesium salts soluble in alcohol other than the chloride, are the magnesium salts recommended as producing the maximum of fire resistant effect with the minimum addition of salt.

Where the transparency of the pyroxylin material is of secondary consideration, calcium or ferric oxalates,[9] sodium or potassium oxalates,[10] or ammonium oxalate[11] have been brought forward as desirable bodies acting harmoniously with pyroxylin for diminishing the inflammability. Certain oxalic esters as diethyl oxalate should be useful for this purpose, although they hydrolyze readily in the presence of moisture. Urea oxalate has been brought forward by J. Hamilton as a useful addition to the cellulose esters for this purpose,[1] while J. Skoglund[2] has found the inflammable action of nitrocotton is materially moderated by the addition thereto of a mixture of ammonium carbonate, oxalate and carbamate. The truth is that commercial ammonium carbonate always contains variable amounts of ammonium carbamate as a product of its decomposition, "effloresced" ammonium carbonate consisting essentially of the carbamate. A mixture of sodium oxalate and bicarbonate has been patented for this purpose.[3]

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[1] Belg. P. 184456, 1905. In this connection see E. Clement, F. P. 402569, 1909 (addition of ethyl or methyl silicates); E P. 10320, 1910; abst. Kunst. 1912, **2**, 17; Span. P. 47917; Belg. P. 225222.

[2] D. Lance, Belg. P. 234302, 1911.

[3] U. S. P. 237279, 245952, 1881.

[4] F. P. 298781, 1900; abst. Mon. Sci. 1901, **57**, 57. Belg. P. 147946, 1900; 158179, 1901. See also N. Erfind. Erfahr. 1902, **29**, 122.

[5] E. P. 11456, 1898; abst. J. S. C. I. 1898, **17**, 631, 1899, **18**, 427, 602.

[6] F. P. 328054, 1902, and additions 1304, 1775; abst. J. S. C. I. 1903, **22**, 1254; Mon. Sci. 1904, **61**, 76.

[7] H. Lagneau, E. Nebel and M. Vignes, F. P. 360912, 1905; abst. J. S. C. I. 1906, **25**, 556; C. A. 1907, **1**, 1501; Mon. Sci. 1907, **67**, 35; 1908, **69**, 656; Chem. Zts. 1906, **5**, 206.

[8] S. de Medveczky, Swiss P. 58686, 1911. See also Fitzgerald, E. P. Appl. 25140, 1919; abst. J. S. C. I. 1919, **38**, 848-A.

[9] A. Mabille and G. Leclerc, F. P. 317884, 1902; and addn. 333 thereto; abst. Mon. Sci. 1903, **59**, 120; 1908, **68**, 655; J. S. C. I. 1902, **21**, 1409.

[10] W. Greaves and E. Hann. E. P. 24847, 1895; abst. Arms & Explo. 1897, **5**, 83; Mon. Sci. 1897, **50**, 168, 1898, **52**, 95; Chem. Ztg. 1897, **21**, 449.

[11] C. Claessen, E. P. 21147, 1911; abst. Chem. Ztg. Rep. 1912, **36**, 483; Zts. Schiess. Spreng. 1912, **7**, 420; J. S. C. I. 1912, **31**, 663; C. A. 1913, **7**, 1100.

The admixture of cellulose acetate with the corresponding nitrate has also been proposed to diminish the inflammability of the latter, as has been described by J. Schmerber and L. Morane[4] and B. Oddo,[5] the latter having described the definite compounds tetracetyloctonitrocellulose, and dinitroacetylcellulose of diminished burning capacity. I. Kitsee[6] adds sulfur and ammonium sulfate to nitrocellulose; Meister, Lucius & Brüning incorporate certain aromatic derivatives of sulfuric acid.[7]

Triphenyl phosphate described elsewhere herein, combines a well defined solvent action for both cellulose nitrate and acetate, is relatively insoluble in water, of negligible hygroscopicity, and a valuable plasticizing and fire-reducing adjunct to pyroxylin. W. Lindsay and the Celluloid Co. employ it in conjunction with 1.5% urea for a combined stabilizer and inflammability reducer. A. Masche[8] renders paper incombustible by triphenyl phosphate and tricresyl phosphate. Trinaphthyl phosphate is less suitable.

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[1] J. Hamilton, E. P. 22162, 1896; abst. Chem. Ztg 1898, **22,** 189; Mon. Sci. 1898, **52,** 178; J. S. C. I. 1896, **15,** 764; 1897, **16,** 716, 825.

[2] E. P. 18362, 1888; abst. J. S. C. I. 1889, **8,** 478; Proc. U. S. Nav. Inst. 1889, **15,** 498; Chem. Ind. 1889, **12,** 416; Chem. Tech. Rep. 1889, **28,** I, 184. See also H. Schöneweg, E. P. 1591, 1888; abst. J. S. C. I. 1889, **8,** 61; Wag. Jahr. 1889, **35,** 478.

[3] Krupp Akt -Ges. E. P. 16617, 1909. See also A. Arent (E. P. 138641, 1920; abst. C. A. 1920, **14,** 1879) for the use of amyl acetate solutions of antimony chloride for fireproofing celluloid, etc.

[4] F. P. 324121, 1902; abst. J. S. C. I. 1903, **22,** 569; Chem. Zts. 1903, **2,** 347.

[5] Gazz. chim. ital. 1919, **49,** II, 140; abst. C. A. 1920, **14,** 1530.

[6] U. S. P. 900744, 1908. See also G. Galy, F. P. 400285, 1909. Cf. Anglo-French F. & S. Ltd., and J. Edwards, E. P. 24025, 1907; abst. J. S. C. I. 1909, **28,** 221. E. P. 10062, 1912.

[7] Belg. P. 144234, 1899; 148560, 1900. E. P. 15355, 1899; abst. Mon. Sci. 1901, **57,** 127; Chem. Ztg. 1900, **24,** 1069; J. S. C. I. 1899, **18,** 811; 1900, 585, 682.

[8] S. Hoggson and G. Pettis, U. S. P. 245952, 1881, recommend aluminium sulfate or steatite in fine powder; G. de Briailles, E. P. 8542, 1908, mechanical combination with gelatin (preferably), chondrin; E. Cadoret and E. Delgraide (E. P. 21485, 1892; abst. J. S. C. I. 1893, **12,** 779) add "camphogine," which is obtained by decomposing turpentine by HCl gas, adding zinc, and boiling with an alkali, when complete incombustibility, it is claimed, is

When nitrocellulose or celluloid is ignited, the heat of combustion is sufficient to raise the surrounding portions to ignition temperature, the result being that the combustion of the mass proceeds throughout its entire substance. If there is incorporated a non-combustible or difficultly burnable constituent, then the ignition of the pyroxylin mass becomes more difficult in proportion to the mass of the non-combustible component. The initial combustion of the cellulose ester mass causes the evolution of heat which is partially dissipated by radiation, and partially consumed in heating up the balance of the mass.

When pure nitrocellulose or celluloid is used, the heat evolved is sufficient for combustion to spread throughout the mass, but with other bodies present there is a diffusion of the heat, and a portion is used in heating the non-combustible portion, with the result that the liability of the entire mass being heated to the ignition point is correspondingly diminished. The total effect, however, is directly dependent on the mass of inert substance and its nature.

While it is true that the addition of a large amount of inert

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obtained; L. Béthisy and M. Rose et Cie., F. P. 347303, 1904; abst. Mon. Sci. 1906, **65**, 112; Chem. Zts. 1905, **4**, 89; C. A. 1907, **1**, 358; J. S. C. I. 1905, **24**, 344, whose process is described as follows: Cellulose, 3, is acted upon by a mixture of nitric acid of 42°, 24, and sulfuric acid of 66° Bé., 56. This mixture is allowed to react for twenty-five minutes, is then washed, dried, etc., and bleached with a mixture of calcium chloride 100 k., aluminium sulfate 60, magnesium sulfate 23, and water 2000 l. A solution of citric acid (citric acid 50 and alcohol of 90% 100) 20, and oil d'aspic 5, is introduced into a ground mixture of crystallized zinc chloride 75. This is finally dissolved in: Amyl acetate 2,700, ether 15, alcohol of 90% 7500, crystallized acetic acid 800, calcium chloride dissolved in its own weight of alcohol of 90%, 20. C. Hagemann and T. Zimmerman (U. S P. 657535, 1900; D. R. P. 99577, 1900; abst. Wag. Jahr. 1898, **44**, 1203; Chem. Centr. 1899, **70**, I, 80; Chem. Ztg. 1898, **22**, 980; Zts. ang. Chem. 1898, **11**, 1153; Jahr. Chem. 1898, **51**, 1382; Mon. Sci. 1899, **54**, 56) dissolve wet nitrocellulose (containing about 50% water) in acetone to a semifluid mass. A concentrated aqueous solution of a salt of a metal—as, for instance aluminium sulfate—is gradually incorporated with the mass by trituration or kneading, to obtain a homogeneous and transparent plastic. An alkali, as caustic soda, is then gradually incorporated with the compound until neutralization—which can be readily seen by the fact that the mass becomes suddenly crumbly and friable, aluminium hydroxide being precipitated—has been completed, the product being known in this state as "hydrocellite." This consists essentially of aluminium hydrate, sodium sulfate, nitrocellulose and water. The sodium sulfate is removed by washing, the mass dried and incorporated with camphor to form a commercial, workable plastic. One point of advantage of this material is that the density and degree of hardness may be varied within wide limits, and that the drying is fraught with no danger.

substance will reduce the probability of the balance of the mass igniting, it is also equally true that the product will be further removed from nitrocellulose in its desirable properties, unless some substance be employed which closely resembles nitrocellulose in its physical deportment. Such a material has as yet, not been found.

The heat of combustion may be further attenuated by making it *do work*, so that the "heat energy" is utilized in initiating chemical reactions. The class of substances of this type can be decomposed on the application of heat, and are thus exothermic in their character, in that they require the expenditure of energy to decompose them, and are incapable of decomposition unless the supply of energy is maintained. A variety of these substances has been used for this purpose, as has been stated above. Some substances as the carbonates, oxalates and ammonium compounds evolve gases on heating, which do not support combustion, and continued ignition is thereby inhibited or checked by limiting the supply of air.

It appears probable that the effect of reducing the inflammability of the nitrated celluloses by the addition of many metallic salts and certain oxides is principally attributable to their presence in sufficient amount to reduce the temperature of combustion below ignition point. With salts such as the inorganic haloids, boric acid, silica and salts of tungsten and molybdenum which have been used for this purpose, little or no decomposition ensues provided the mass is kept dry. The addition of such materials as gelatin, resins, metallic oleates, palmitates and stearates, presumably owe their effect to the relatively large amount of heat necessary to decompose them. A comprehensive classification of these bodies is difficult, however, as but little tangible datum seems to have been recorded as to the calorimetric problems connected with the combustion of nitrocellulose, and the so-called inflammable celluloid.

The term *non-inflammable* as applied to celluloid in this connection is decidedly ambiguous and somewhat of a misnomer, since the substances added only tend to raise the temperature of ignition and dissipate the heat evolved on combustion. The question of non-inflammability is primarily one of comparison—a relative expression—and no nitrocellulose product, however treated, can properly be termed non-inflammable.[1] A better term, perhaps, would be *less* or *difficultly* inflammable.

Several writers have claimed that nitrocellulose or celluloid to which has been added other inert and inorganic substances in amounts sufficient to materially decrease the flammation, should properly not be considered as cellulose nitrate or celluloid, but rather as a profoundly modified product, and their reasoning appears logical. So many seemingly unimportant points have to be taken into consideration in the selection and incorporation of a product designed to diminish the inflammability in the cellulose nitrates, in order that the valuable properties of moldability, thermoplasticity, solubility, elasticity and elongation, viscosity, tensile strength, enduring stability and transparency be substantially conserved, that the successful solution of the problem has been exceedingly difficult. In fact, its elucidation is still in the future. It is one thing to materially reduce the inflammability, but quite another and much more difficult procedure to have conserved the valuable properties of the cellulose ester after doing so.

Ballistics of Nitrocellulose. The general subject of the ballistics of smokeless powders and nitrocellulose containing explosives forms a separate chapter in Volume VII of this series. In this topic is touched upon some of the principles connected with the ballistics and the thermal considerations of the cellulose nitrates only, reserving their treatment *in extenso* for Volume VII.

As early as 1847 C. Combes[2] conducted quite elaborate ballistic and blasting experiments with guncotton, which was followed by the investigations of G. Clark[3] and H. Sebert.[4] It was early found[5] that guncotton could be detonated, and will develop greater power in that manner, and M. v. Förster[1] showed conclusively that guncotton containing 25% of water has a stronger action than when dry, when used in the open, while increasing the specific gravity tends to the same effect. He reports an experiment in which a lead cylinder filled with nitrocellulose and detonated, showed six times greater force at the point where the detonating cap had been placed.

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[1] D. R. P. 267407, 1913; abst. C. A. 1914, **8,** 1011; Chem. Ztg. Rep. 1913, **37,** 686; Wag. Jahr. 1913, **59,** II, 502; Zts. ang. Chem. 1914, **27,** 25. W. Lindsay and the Celluloid Co. stabilize with 1.5% urea in conjunction, preferably with triphenyl phosphate, as shown by their patents: U. S. P. 1050065, 1913; abst. J. S. C. I. 1913, **32,** 133; Kunst. 1913, **3,** 218. D. R. P. 263056, 1910; abst. Kunst 1913, **3,** 375. See also E. P. 10794, 1910; abst. J. S. C. I. 1911, **30,** 679. F. P. 415517, 1910; abst. J. S. C. I. 1910, **29,** 1299; Mon. Sci. 1912, **77,** 9. E. P. 10795, 1910; abst. J. S. C. I. 1911, **30,** 205. F. P. 418518, 1910; abst. J. S. C. I. 1910, **29,** 1299; Mon. Sci. 1912, **77,** 9. U. S. P. 1045990, 1913; abst. J. S. C. I. 1913, **32,** 19; C. A. 1913, **7,** 699. U. S. P. 1067785, 1913; abst. J. S. C. I. 1913, **32,** 823; C. A. 1913, **7,** 3025.

[2] Compt. rend. 1848, **26,** 61; Dingl. Poly. 1848, **108,** 141; abst. Jahr. Chem. 1847–1848, **1,** 1144.

[3] Amer. Chemist, 1870, **1,** 436.

[4] Mem. poud. salp. 1882, **1,** 109.

[5] See Deut. Industrieztg. 1869, 178; Dingl. Poly. 1869, **192,** 165;

L. Troost and P. Hautefeuille,[2] in determining the heat of combustion of nitrous and nitric acid with various compounds, showed that one equivalent of guncotton is equal to 52000 heat units. A. Vogel[3] proved the presence of nitric and nitrous acid in the combustion of guncotton by burning in a cylinder, and aspirating through starch iodide and also litmus solutions. G. McRoberts,[4] in determining the force of disruption of various explosives, found that "dinitrocellulose" gives an energy in foot pounds of 550.

M. Berthelot[5] has determined the speed of transmission of the explosion waves for various substances and including guncotton, the latter, in lead tubes with a density of loading of 0.9–1.2, giving 3903 to 4267 meters per second; in tin tubes, density, 1.4, 4818–6238 m. per second. The heat of formation of guncotton[6] was found equivalent to 919 calories per gram (549

Industriebl. 1869, **93**; Poly. Notizbl. 1869, **24**, 156; Wiederhold's Gewerbebl. 1869. 59; Chem. Tech. Rep. 1869, **8**, I, 103.

[1] Dingl. Poly. 1883, **250**, 466; 1884, **251**, 371; 1886, **261**, 25; 188, **269**, 240; Chem. News, 1885, **52**, 185; J. C. S. 1884, **46**, 948; J. S. C. I. 1884, **3**, 329, 330; 1886, **5**, 502; Van Nostrand's Engrg. Mag. 1884, **31**, 113; Proc. U. S. Nav. Inst. 1885, **11**, 109; 1886, **12**, 563; 1889, **15**, 513; Chem. Ind. 1884, **7**, 133; Chem. Tech. Rep. 1884, **23**, I, 200; 1886, **25**, I, 158; II, 296; Chem. Ztg. 1884, **8**, 348; 1886, **10**, 530; Jahr. Chem. 1884, **37**, 1750; 1886, **39**, 2077; Wag. Jahr. 1886, **32**, 324; Pop. Sci. Mon. 1888, **32**, 133.

[2] Compt. rend. 1871, **73**, 378; Bull. Soc. Chim. 1871, **16**, 218; Zts. Chem. 1871, **14**, 344; Jahr. Chem. 1871, **24**, 82; J. C. S. 1871, **24**, 871.

[3] N. Rep. Pharm. **24**, 723; abst. Jahr. Chem. 1875, **28**, 153.

[4] J. S. C. I. 1890, **9**, 265, 476; abst. Zts. ang. Chem. 1890, **3**, 492; Wag. Jahr. 1890, **36**, 541; Chem. Ztg. 1890, **14**, 379; Chem. Tech. Rep. 1890, **29**, I, 225; II, 146; Jahr. Chem. 1890, **43**, 2705, 2708; Tech. Chem. Jahr. 1890–1891, **13**, 156, 161, 171; Dingl. Poly. 1890, **278**, 418; Mon. Sci. 1891, **37**, 391; Bull. Soc. Chim. 1891, **6**, 518, 521; Rev. chim. ind. 1891, **2**, 267; Chem. Ind. 1891, **14**, 74.

[5] Compt. rend. 1885, **100**, 314; Ann. Chim. Phys. 1885, **6**, 556; abst. Proc. U. S. Nav. Inst. 1886, **12**, 188; Amer. J. Sci. 1886, **31**, 149; J. A. C. S. 1885, **7**, 93; Chem. News, 1885, **51**, 142; Jahr. Chem. 1885, **38**, 179; Mon. Sci. 1885, **27**, 312; Rev. Sci. 1885, **35**, 248; Dingl. Poly. 1885, **256**, 408; J. S. C. I. 1885, **4**, 509; Bull. Soc. Chim. 1885, **43**, 536; Ber. 1885, **18**, 135-R; J. C. S. 1885, **48**, 478; Rev. Ind. 1885, 188; Wag. Jahr. 1885, **31**, 295.

[6] Ann. Chim. Phys. 1876, **9**, 145, 161; abst. Jahr. Chem. 1876, **29**, 99; Wag. Jahr. 1878, **24**, 467.

gm. gave 502000 cal.). He[1] states the heat of combustion of nitrocellulose to be 55000; nitromannite, 21200; and nitrostarch, 12000 calories respectively.

C. Goettig[2] in investigating the chemical processes which take place on the decomposition of nitro-compounds, has given the composition of the gases of combustion of guncotton, but his results have been taken exception to by later experimenters. The velocity of detonation in meters per second of dry guncotton is given as 3900 for 0.9 density, 4300 for 1.2 density, and 4800-6200 for 1.4 density, while wet with 15% water, the velocity has been given as 5500-5800. Nitromannitol of 1.5 density gives under the same conditions, 7000; and 1.9 density, 7700.

W. Macnab and A. Leighton,[3] in the analysis of a number of smokeless powders, give the following results: for Walsrode powder consisting of practically pure nitrocellulose (98.6% n.c., 1.4% volatile matter): calories per gm., 1014; permanent gas, cc. per gm. 669; aqueous vapor, cc. per gm. 206; total volume of gas at 0° and 760 mm. 875; composition of permanent gas, CO, 48.2%; CO_2, 21.3%; CH_4, 0.4%; H, 10.1%; N, 14.8%.

According to E. Sarrau and P. Vieille,[4] the combustion of organic compounds which do not contain sufficient oxygen for complete oxidation, like the cellulose nitrates, results in the formation of a state of equilibrium between the gaseous products, some of which are completely oxidized as CO_2 and H_2O, while in others as CO, H_2 and CH_4, oxidation is incomplete. Their experiments have shown that the conditions of final equilibrium change with an increase in the weight of substance exploded in the same space, i. e., with an increase in the pressure produced by the products. Two principal reactions are concerned in the progressive alteration of equilibrium. The first $CO + H_2O + H_2$, usually occurs, but $2CO + 2H_2O + CO_2 + CH_4$, takes place when the first has reduced the proportion of water vapor and increased that of free hydrogen to a certain extent, or when the explosive contains such a relatively small amount of oxygen that water is formed in small quantity. The authors find this first reaction to take place with a nitrocellulose of $C_{24}H_{29}N_{11}O_{42}$, their results being:

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[1] Compt. rend. 1871, **73**, 260; Bull. Soc. Chim. 1871, **16**, 223; abst. Zts. Chem. 1871, **14**, 345; Jahr. Chem. 1871, **24**, 81; Rev. Sci. 1871, **8**, 286; J. C. S. 1871, **24**, 872. M. Berthelot and P. Vieille, Ann. Chim. Phys. 1883, **28**, 289, 332; Bull. Soc. Chim. 1883, **40**, 353; Compt. rend. 1883, **96**, 672; Jahr. Chem. 1883, **36**, 151.

[2] Ber. 1898, **31**, 25; abst. J. S. C. I. 1898, **17**, 271; J. C. S. 1898, **74**, i, 244; Chem. Centr. 1898, **69**, I, 538; Jahr. Chem. 1898, **51**, 1383; Wag. Jahr. 1898, **44**, 381; Bull. Soc. Chim. 1808, **20**, 642; Mon. Sci. 1898, **51**, 504; Tech. Chem. Jahr. 1898-1899, **21**, 146.

[3] J. S. C. I. 1904, **23**, 298; abst. Jahr. Chem. 1904, **57**, 819; Chem. Centr. 1904, **75**, I, 1677.

[4] Compt. rend. 1887, **105**, 1222; abst. Jahr. Chem. 1887, **40**, 47; Wag. Jahr. 1888, **34**, 501; Zts. ang. Chem. 1888, **1**, 59; Tech. Chem. Jahr. 1887-1888, **10**, 202; J. C. S. 1888, **54**, 339.

Density of Gas		Methane
0.010	$33CO + 15CO_2 + 8H_2 + 11N_2 + 21H_2O$,	0.00
0.023	$30CO + 18CO_2 + 11H_2 + 11N_2 + 18H_2O$,	0.00
0.200	$27CO + 21CO_2 + 14H_2 + 11N_2 + 15H_2O$,	0.006
0.300	$26CO + 22CO_2 + 15H_2 + 11N_2 + 14H_2O$,	0.016

The temperature of final equilibrium is about 3000°, the pressure varying between 100 and 4000 atmospheres.

They have also studied the decomposition of ordinary guncotton[1] under various conditions, and find that at pressures near that of the normal atmosphere, the whole of the nitrogen is eliminated as nitric oxide, but at higher pressures it is reduced, and the sole products of combustion are N_2, H_2, CO, CO_2 and H_2O, the proportion of carbon monoxide and water decreasing with increase of pressure, while that of the carbon dioxide and hydrogen increases. The heat of combustion of guncotton was found to be 1070 cals. per kilo, and the heat of formation 542 per kilo, or 620 per equivalent.

P. Champion and H. Pellet[2] made extensive experiments on the explosion of wet guncotton by means of mercury fulminate caps, as well as the influence of starch on the explosibility. Comparison of wet guncotton with a nitro explosive such as picric acid, shows that the former is relatively sensitive to shock. The liability of dry guncotton to explode on striking or by rough handling is undoubtedly the cause of many explosions in which this material has been used.

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[1] Compt. rend. 1879, **89**, 165, 169; 1880, **90**, 1058, 1112; 1881, **93**, 269; abst. Chem. News, 1879, **40**, 89; 1880, **41**, 273, 282; **42**, 282; J. A. C. S. 1879, **1**, 399; 1880, **2**, 435; J. C. S. 1880, **38**, 780; 1881, **40**, 342, 483; Bull. Soc. Chim. 1880, **33**, 581; **34**, 556; Mon. Sci. 1879, **21**, 958; 1880, **22**, 680, 686; Rev. Sci. 1879, **24**, 117; Ber. 1879, **12**, 2157; 1880, **13**, 1369, 1477; Chem. Centr. 1880, **51**, 391; Chem. Ind. 1879, **2**, 322; Chem. Tech. Rep. 1879, **18**, II, 218; Dingl. Poly. 1879, **233**, 494; 1880, **237**, 253; Jahr. rein Chem. 1880, **8**, 31; Jahr. Chem. 1879, **32**, 1116; 1880, **33**, 127, 1303, 1304, 1881, **34**, 1131; Wag. Jahr. 1879, **25**, 419; 1880, **26**, 380. J. C. S. 1881, **40**, 342, 968. See also Rev. Sci. 1881, **28**, 190, 221.

[2] Compt. rend. 1875, **81**, 982; abst. Jahr. Chem. 1875, **28**, 1076; Jahr. rein Chem. 1875, **3**, 456; Chem. Tech. Rep. 1875, **14**, II, 218; Bull. Soc. Chim. 1875, **24**, 439; Amer. Chemist, 1876, **6**, 232; Mon. Sci. 1876, **18**, 193; Wag. Jahr. 1876, **22**, 480; See also Jahr. Chem. 1876, **29**, 101; J. C. S. 1877, **30**, 228.

L. von Karolyi[1] and W. Macnab and E. Ristori[2] have determined the decomposition of guncotton, the former using a decanitrocellulose, and the latter an ester of 13.3% N.

	Karolyi	Macnab and Ristori
Carbon dioxide	20%	29 27%
Carbon monoxide	30%	38.52%
Methane........	10%	0 24%
Hydrogen......	. . .	0.24%
Nitric oxide..........	9%	....
Nitrogen.............	8%	13 60%
Water......	28%	16.30%

C. Bichel[3] obtained gases of about the same composition as those found by Macnab and Ristori. Assuming that the water is not condensed, one kilo of guncotton gives about 875 liters of gas reduced to normal temperature and pressure, according to Bichel. Various equations have been proposed to represent the decomposition of nitrocellulose, but it is stated by Bichel that a satisfactory equation is not possible, as the conditions of the individual experiment have an influence on the composition of the various products. E. Sarrau and P. Vieille state[4] that in all instances where the explosive does not contain sufficient oxygen

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1. Wien. Akad. Ber. **47**, 59; Pogg. Ann. Phys. 1863, **118**, 544; Poly. Centr. 1863, **29**, 996; Dingl. Poly. 1863, **168**, 158; **169**, 426; abst. J. prakt. Chem. 1863, **90**, 129; Wittstein's Vierteljahrschr. 1864, **13**, 73; Chem. Centr. 1863, **34**, 596; Jahr. Pharm. **19**, 313; Wag. Jahr. 1863, **9**, 304; Bull. Soc. Chim. 1863, **5**, 613; Poly. Notizbl. 1863, **18**, 112; Jahr. Chem. 1863, **16**, 744; Phil. Mag. 1863, **26**, 266.
2. Proc. Roy. Soc. 1900, **66**, 221; abst. J. S. C. I. 1900, **19**, 467; Jahr. Chem. 1900, **53**, 615. See also Proc. Roy. Soc. 1894, **56**, 8, 19; abst. J. S. C. I. 1894, **13**, 973; J. C. S. 1895, **68**, ii, 434; Jahr. Chem. 1894, **47**, 293; Wag. Jahr. 1895, **41**, 472; Ber. 1895, **28**, 1018; Mon. Sci. 1895, **45**, 148; Mitth. Gegenst. Artill. Geniew. 1894, 93; Arms & Explo. 1894, **2**, 178, 193.
3. Zts. Berg. u. Hüttenw. 1902, 669; Glückauf, 1905, **41**, 1194; Marine Rundschau, 1905, 1345; Zts. Schiess. Spreng. 1906, **1**, 13, 14, 31, 155, 178; 1908, **3**, 340, 365, 393, 403; abst. C. A. 1909, **3**, 1214; Mon. Sci. 1906, **64**, 849; Meyer Jahr. Chem. 1906, **16**, 328; 1908, **18**, 308; Tech. Chem. Jahr. 1905, **28**, 205, 206; Wag. Jahr. 1902, **48**, I, 369, 370, 371; 1906, **52**, I, 497; 1908, **54**, I, 454.
4. Compt. rend. 1887, **105**, 1222; abst. Jahr. Chem. 1887, **40**, 47; Wag. Jahr. 1888, **34**, 501; Zts. ang. Chem. 1888, **1**, 59; Tech. Chem. Jahr. 1887-1888, **10**, 202; J. C. S. 1888, **54**, 339.

for complete combustion, that an equilibrium may be reached between the gaseous products, the equilibrium being affected by the density of the charge. If the cellulose nitrate is burned in an excess of oxygen or air, the products of decomposition are entirely different.

There also appears to be trustworthy evidence for believing that the products as determined with the cooled gases are different from those liberated at the moment of explosion. O. Poppenberg and E. Stephan[1] consider that the difference in composition of the gas primarily due to the density of loading can be ascribed to secondary reactions. With high density of loading there is a larger amount of heat to be conducted away through the same surface, consequently the cooling is retarded. There is then a greater opportunity for the initiation of secondary reactions to take place, than when the products are cooled.

In 1895 A. Noble (not A. Nobel) published his experiments[2] showing the transformation during explosion, and the pressure developed, when guncotton and smokeless powders, are fired in a closed vessel. The following tables show the effect of pressure on the composition of the resulting gases, when guncotton is fired under different conditions, the amount of CO_2 increasing with the pressure.

Under a pressure of about 10 tons per square inch, strand guncotton developed 1068 calories (water fluid), 689 cc. of permanent gas, and 162.6 cc. of aqueous vapor, per gm. at 0° and 760 mm. pressure.

In a subsequent research,[3] the object of which was to ascer-

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[1] Zts. Schiess. Spreng. 1909, **4**, 281, 305, 388; 1910, **5**, 266, 291, 310, 452, 474; abst. C. A. 1910, **4**, 1675, 3139; 1911, **5**, 1515; J. S. C. I. 1910, **29**, 1083; Chem. Zentr. 1909, **80**, II, 1506; 1910, **81**, II, 1004; 1911, **82**, I, 851; Jahr. Chem. 1909, **62**, I, 149; 1910, **63**, I, 644; Meyer Jahr. Chem. 1909, **19**, 331; 1910, **20**, 326; Wag. Jahr. 1909, **55**, I, 435, 437, 447; 1910, **56**, I, 500. See also H. Kast, Zts. Schiess. Spreng. 1910, **5**, 205, 248, 376, 399; abst. C. A. 1910, **4**, 2877; J. S. C. I. 1910, **29**, 1273; Chem. Zentr. 1910, **81**, II, 770, 1960; Jahr. Chem. 1910, **63**, I, 643; Meyer Jahr. Chem. 1910, **20**, 326; Wag. Jahr. 1910, **56**, I, 500.

[2] Proc. Roy. Soc. 1894, **56**, 205; abst. J. S. C. I. 1895, **14**, 185; Rev. Sci. 1894, (4), **1**, 251.

[3] Proc. Roy. Soc. 1905, **76A**, 381, 512; 1906, **78A**, 218; Trans. Roy. Soc. 1906, **206A**, 453; abst. Arms & Explo. 1906, **14**, 160; J. S. C. I. 1905, **24**, 940; 1906, **25**, 40, 1003; Chem. Centr. 1905, **76**, II, 995; 1906, **77**, II, 311, 1887; Jahr. Chem. 1905-1908, II, 980; Meyer Jahr. Chem. 1905, **15**, 359. See also La Nature, 1900, **62**, 86, 111; abst. Wag. Jahr. 1900, **46**, I, 409.

TABLE CXXXIII.—RESULTS IN VOLUMES OF THE ANALYSES OF THE PERMANENT GASES GENERATED BY THE EXPLOSION OF STRAND GUNCOTTON, ARRANGED ACCORDING TO ASCENDING PRESSURES

Under Pressure of Gas		Tons per Square Inch										
		1 5	2.5	8 0	8.0	12.0	12.3	18 0	20 0	45.0?	48.0?	50.0?
CO_2	(vols)	26 49	29.62	30.95	31.00	32.23	32.70	33.63	33.01	34.70	34.77	36.18
CO	"	36.66	35 03	32 27	32.76	30 65	31.36	31.20	30.32	28.60	28.66	27 57
H	"	19 68	17.13	19.10	18 80	20 38	19.23	17.99	18 25	16.56	17 48	16.76
N	"	16 85	18.18	17 20	16.90	16 43	16 25	16 23	16 60	16.83	16.05	16.15
CH_4	"	0 32	0.04	0 48	0.54	0 31	0 46	0 95	1 82	3.31	3.04	3.34

TABLE CXXXIV.—RESULTS IN VOLUMES OF THE ANALYSES OF THE PERMANENT GASES GENERATED BY THE EXPLOSION OF PELLET GUNCOTTON, ARRANGED ACCORDING TO ASCENDING PRESSURES

Under Pressure of Gas		Tons per Square Inch									
		1 0	1.5	6.5	11.0	14.0	15.0	17.0	17.0	25.0	30.0
CO_2	(vols)	21 50	25.03	25 61	26.68	27.41	25.75	28.54	28 39	28 24	28.88
CO	"	39 70	36.85	39.51	36 97	37.23	38 00	35.52	36.41	34.94	35.64
H	"	22 83	21 00	18.80	19 59	19 37	19.71	18.47	19.64	20.30	20.50
N	"	15.58	15.88	15.97	15 91	15 35	15.26	16 08	14.90	15.59	14.98
CH_4	"	0 39	1 24	0.11	0 85	0 64	1.28	1.39	0 66	0.93	.....

TABLE CXXXV.—ANALYSIS OF STRAND AND PELLET GUNCOTTON WHEN FIRED IN A CLOSED VESSEL BY DETONATION

	Strand Guncotton Pressure* per Square Inch		Pellet Guncotton Pressure per Square Inch	
	1 ton	3 tons	3 tons	10 tons
CO_2 (vols.)......	19.21	29.08	25.76	26.50
CO (vols.)......	41.25	32.88	39.34	37.48
H (vols.).......	23.07	20.14	18.71	20 97
N (vols.)........	16.21	17.50	16.19	15.05
CH_4 (vols.)......	0 26	0.75	None	None

* The pressures given are those due to the gravimetric density of the charge.

tain the differences in transformation which modern explosives suffer when fired under gradually increasing, but considerable differences in pressure, cordite Mark I, cordite MD, and nitrocellulose (known as R. R. Rottweil) were studied, the results obtained with the latter being shown in the following table:

TABLE CXXXVI.—NITROCELLULOSE

Density of charge exploded......	....	0.05	0.222	0.45
Volume of permanent gas per gm.	....	814 7	759 2	680.9
Volume of total gas per gm ...	....	993 1	922 3	816.3
Percentage volume of permanent gases.............. ..	CO_2	17.90	25.10	35 00
	CO	43.45	36 55	27.85
	H	24.40	20.25	12.65
	CH_4	0.60	4 70	11.10
	N	13 65	13 40	13.40
Percentage volume of total gases	CO_2	14.68	20.66	29 16
	CO	35.63	30.09	23.20
	H	20.01	16.67	10.54
	CH_4	0 49	3.87	9.25
	N	11.19	11.03	11.16
	H_2O	18.00	17.68	16 69
Pressure in tons per sq. in......	....	3 35	16.47	40 5
Units of heat (water fluid)......	....	896.1	931.0	1036.9
Temperature of explosion, ° C..	....	3488.1	3667.7	4282.9
Comparative potential energy...	....	0.7389	0.7438	0.7686

Holborn and Austin[1] have shown that the specific heats of carbon dioxide increases with rise of temperature, the increments gradually becoming smaller. It is assumed from extrapolation that the specific heat at constant volume becomes constant at 1300°, viz., 0.2111. The temperature of explosion of nitrocellulose when calculated by A. Noble on this basis,[2] and also from he pressure, assuming the following law to hold:—$t = \dfrac{p + p^\circ}{0.00367p^\circ}$ ives the following values:

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[1] Sitzber. Preuss. Akad. Wiss. Berlin, 1905, **5**, 175; abst. J. C. S. 1905, **88**, ii, 228; Chem. Centr. 1905, **76**, I, 713; Jahr. Chem. 1905–1908, I, 369; J. S. C. I. 1906, **25**, 40.

[2] Proc. Roy. Soc. 1905, **76A**, 512; abst. J. S. C. I. 1906, **25**, 40.

Density of Charge	CORDITE Temp. from Pressure	CORDITE Temp. from Sp. Heat	CORDITE M. D. Temp. from Pressure	CORDITE M. D. Temp. from Sp. Heat	NITROCELLULOSE Temp. from Pressure	NITROCELLULOSE Temp. from Sp. Heat
0.50	5275	5263	....	....	....	....
0.45	5090	5090	4713	4624	4305	3954
0.40	4902	4970	4494	4411	4007	3890
0.35	4710	4860	4200	4215	4630	3795
0.30	4480	4800	3920	4070	3320	3670
0.25	4165	4770	3585	3945	3060	3530
0 20	3838	4760	3240	3870	2835	3425
0.15	3490	4760	2890	3840	2680	3345
0.10	3140	4790	2530	3830	2520	3295
0.05	2775	4800	2160	3860	2400	3255

In the fourth of his researches on explosives, A. Noble,[1] has recorded results with R. R. Rottweil nitrocellulose (containing 85.5% soluble, and 14.5% insoluble ester), the temperature of formation of the nitrocellulose being 3200°, while the percentage of CO_2 found was but 19.45%. The specific heat of the gases composing the products of explosion may be taken as approximately 0.28. If blasting gelatin (8% collodion cotton) is taken as 100 for the lead block test and 100 according to the energy content, then guncotton gives similar values of 29 and 54 respectively. Where the density of loading of guncotton is 1.25, the velocity of detonation in meters per second is given as 6383, and the concussive energy in sec./kgm./meters as 2076589. The dynamic concussive energy of an explosive is one of its most important characteristics.

C. Munroe[2] reports an instance of a cast iron shell charged with wet guncotton, which upon firing in sand, fused or sintered the surrounding sand in the form of a tube resembling *fulgurites.* The experiments of L. Roux and E. Sarrau[3] indicate 1056.3 heat units C. are given off by the explosion of guncotton, this indicating a temperature of 3700°, while Nobel and Abel found 4400°. Berthelot has estimated that guncotton of 1.1 density, exploded in its own volume, will generate a pressure of 100 tons per square inch. The rate of propagation of the explosive wave of guncotton in rigid tubes has been found to be 5000–6000 meters per second. C. Munroe has shown at the naval guncotton factory, Newport, R. I., that thoroughly dry guncotton can be detonated by 3 grains of mercury fulminate; air-dry guncotton by 5 grains if the fulminate be confined in copper tubes, and the tubes are in close contact with the nitrocotton.

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[1] Trans. Roy. Soc. 1906, **206A,** 453; abst. J. S. C. I. 1906, **25,** 1003.

[2] Amer. J. Sci. 1917, **43,** 389; abst. J. S. C. I. 1917, **36,** 669; C. A 1917, **11,** 2043.

[3] Compt. rend. 1873, **77,** 138, 303, 498, Mon. Sci. 1873, **15,** 496 514, 838, 906, 1007; abst. Chem. News, 1873, **28,** 142; Dingl. Poly. 1873 **209,** 303; **210,** 21; Wag. Jahr. 1873, **19,** 346, 352; Les Mondes, 1873 (Aug.) Amer. Chemist. 1874, **4,** 435; Jahr. Chem 1873, **26,** 1028; Rev. Sci. 1873, (2) **3,** 216; J. C. S. 1874, **27,** 119. Compt. rend. 1874, **79,** 757; abst. J. C. S. 1875 **28,** 126. See also Compt. rend. 1874, **79,** 577; abst. Amer. Chemist, 1875 **5,** 428; Poly. Centr. 1874, **40,** 1292; Wag. Jahr. 1875, **21,** 527; Rev. d'Artil 1875, **5,** 349.

The Action of Fungi on Nitrocellulose. T. Bokorny[1] has investigated the action of various fungi and moulds upon nitrocellulose and the nitrated carbohydrates and has found that cellulose tri-nitrate serves as a food supply for moulds when suspended in sterile distilled water containing the requisite mineral matter and kept in the dark. The nitrocellulose appears to serve as a source of carbon, perhaps also as a nitrogen source. When treated with a solution of calcium nitrate, potassium phosphate and magnesium sulfate, fungi developed in large numbers within twelve days which adhered to and distinctly corroded the nitrocellulose fiber. Pure cellulose treated in the same manner and under comparable conditions gave a negative result. Glycerol has been found to retard, if not prevent their growth.

M. Jacque[2] has reported upon the influence of micro-organisms and vegetable acids upon the stability of nitric esters, and concludes that the action of small organisms such as *Micrococcus prodigiosus* and others, which sometimes develop in the storage of collodion and guncotton, does not seem to modify the stability of these substances. He points out, however, the possible effect of certain salts which are necessary to the growth of these bacteria, for, although the regularly manufactured products will never contain them, yet nevertheless, the water used for manufacture may contain sufficient amounts of these salts to exert an appreciable influence. Nitroglycerol and nitroglycerol powders may be considered as antiseptic media, in that living organisms cannot thrive in them. Vegetable and organic matter nevertheless have an indirect action on the stability of nitric esters; the prolonged action of weak acids such as are formed in the first washings of these esters, may possibly be the cause of the formation of unstable products, if the water contains certain organic acids or salts (i. e., oxalic acid) which may be the result of decomposition of vegetable and microscopic living organisms.

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[1] Chem. Ztg. 1896, **20**, 985; abst. Jahr. Chem. 1896, **49**, 1031; Chem. Centr. 1897, **68**, I, 30; J. C. S. 1898, **74**, ii, 39. Cf. T. Bokorny, Pflügers Archives, 1896, **64**, 262; abst. J. C. S. 1896, **70**, ii, 669.

[2] Seventh Intl. Cong. Appl. Chem. 1909, **3B**, 53; Zts. Schiess. Spreng. 1910, **5**, 81; abst. C. A. 1910, **4**, 1546; J. S. C. I. 1910, **29**, 373; Chem. Zentr. 1910, **81**, I, 2147; Zts. ang. Chem. 1910, **23**, 1199.

This fact, verified in the laboratory as evidenced by the experience of a dynamite factory, in which certain difficulties in stabilization were not overcome until the water reservoirs and pipes were cleaned of plants and living organisms contained therein, is an interesting example. Such phenomena prove that the origin and quality of the water employed for the manufacture as well as for the re-stabilization of nitro-explosives that have been altered by time or climate, deserve especial attention, not only because of the fermentation germs possibly contained therein, but more especially on account of the organic salts resulting from the decomposition of vegetable and organic bodies.

Straw Nitrocellulose. As far back as 1859,[1] S. Barnwell and A. Rollason, realized the possible advantages that might accrue from the employment of straw nitrocellulose as a constituent in propellent smokeless powders and in the preparation of waterproof fabrics for umbrellas, parasols, hats and hat covers, capes, caps and mantles. Their work was followed in 1879 by the experiments of E. Judson[2] and of J. Hüter[3] in attempts to prepare stable products by the treatment of straw with a nitrating mixture in the usual manner. J. Lanfrey's powder, which was evolved in 1878,[4] comprized the treatment of straw with nitrating acids to produce a nitrocellulose compound which was afterwards impregnated with a solution containing saltpeter and dextrin and to which the name Straw Dynamite or Paleine was given. The silica naturally present in the straw was claimed to add stability, but on what grounds it is difficult to perceive.

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[1] E. P. 945, 1859. E. P. 2249, 1860. G. Mosander, Berz. Jahr. 1847, **27,** 416 nitrated cut straw. E. Cotte, E. P. 3119, 1878; abst. Wag. Jahr. 1879, **25,** 418 claimed nitrated straw made by his process obtained increased stability from the silica remaining therein. He called his product "Paleine."

[2] D. R. P. 6064; Chem. Tech. Rep. 1879, **18,** I, 290; Wag. Jahr. 1879, **25,** 423; Chem. Ztg. 1879, **3,** 96; Dingl. Poly. 1879, **234,** 253. For study of "straw dynamite," see Bruneau, Mem. Poud. Salp. 1891, **4,** 205.

[3] D. R. P. 3067; abst. Chem. Tech. Rep. 1879, **18,** I, 290; Chem. Ind. 1879, **2,** 50; Dingl. Poly. 1879, **232,** 188; Chem. Centr. 1879, **50,** 448; Ber. 1879, **12,** 208.

[4] E. P. 3119, 1878; abst. Chem. Ztg. 1879, **3,** 463; Industrieblätter, 1879, 275; Wag. Jahr. 1879, **25,** 318; 1883, **29,** 388; Chem. Tech. Rep. 1879, **18,** I, 289; Dingl. Poly. 1879, **234,** 253; 1881, **240,** 407; J. Lanfrey and J.

C. Bjorkmann in 1875,[1] Dolliak in 1882[2] and C. Hengst in 1888,[3] placed upon the market as commercial possibilities, compounds in which nitrated straw was the principal constituent. In the explosive of Bjorkmann—to which the name Vigorite was given—pea meal was combined with sawdust and nitrated oat straw together with a compound called nitroline, made by the action of 80 parts of nitric acid, and 170 parts sulfuric acid on 15 parts of raw stearic acid and 15 parts of syrup. It appears this product did not attain the commercial success claimed for it by the patentee. The nitrated oat straw of Springthorpe[4] and of the Societe Francaise des Explosifs[5] together with the brisant of the Societe Anonyme des Poudre et Dynamites,[6] so far as aware never assumed any distinct commercial importance. In 1912 K. Nitzelnadel,[7] as the result of his experiments on the

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Renard, D. R. P. 12115, 1880; abst. Wag. Jahr. 1881, **27**, 381; Dingl. Poly. 1883, **248**, 427, 509; Jahr. Chem. 1883, **36**, 1703. Mitth. Gegenst. Artill. Geniewesens, 1882, 276; Ber. 1881, **14**, 125. F. P. 124789, 1878; Add. of Dec. 18, 1878; abst. Mon. Sci. 1879, **21**, 1049. Belg. P. 49853. Ital. P. Aug. 17, 1878. Aust. P. 5524. Port. P. June 11, 1879. Swed. P. Aug. 20, 1880.

[1] E. P. 2459, 1875; U. S. P. 177988, 1876; abst. Deut. Industrie Ztg. 1876, 58; Chem. Tech. Rep. 1875, **14**, II, 216; Zts. Chem. Grossgewerbe, 1876, **1**, 233; Chem. Tech. Mith. 1877, **27**, 340.

[2] Mitt. Art. Geniewesens, 1882, 278; Dingl. Poly. 1883, **248**, 509; 1885, **255**, 518; J. S. C. I. 1885, **4**, 366; Chem. Tech. Rep. 1882, **21**, II, 176; 1885, **24**, I, 201; Jahr. Chem. 1883, **36**, 1704; Wag. Jahr. 1883, **25**, 388; Mitthl. Artil. Geniewesens, 1882, 278; Berg. u. hütten Ztg. 1882, 119; Dingl. Poly. 1885, **255**, 523; Chem. tech. Centr. 1885, **3**, 454.

[3] E. P. 13656, 1888; abst. J. S. C. I. 1889, **8**, 478, 1890, **9**, 325; Chem. Tech. Rep. 1890, **29**, I, 222; Chem. Ztg. 1889, **13**, 408; Jahr. Chem. 1890, **43**, 2710; Zts. ang. Chem. 1890, **3**, 247; Wag. Jahr. 1890, **36**, 546. E. P. 16783, 1887; abst. J. S. C. I. 1889, **8**, 818; D. R. P. 48265, 1888; abst. Gewerbebl. Schw. **14**, 364; Iron, **33**, 202; Neuste Erfind. Erfahr. **16**, 554; Mitth. Seew. **17**, 364, 365; Chem. Tech. Rep. 1889, **28**, I, 183; Chem. Ind. 1889, **12**, 416; Chem. Ztg. 1889, **13**, 1266; Jahr. Chem. 1889, **42**, 2679, 2683; 1890, **43**, 2710; Wag. Jahr. 1889, **35**, 473. F. P. 194803, 1888; abst. Mon. Sci. 1889, **34**, 756. His product was called Hengstite.

[4] F. P. 207919, 1890; abst. Mon. Sci. 1891, **37**, 460.

[5] Their preferred compound comprized 50.81 parts nitrated straw, and 49.19 parts nitrotoluol, as an absorbent combination for nitroglycerol.

[6] See this work, Vol. VII. For the nature of the cellulose of cereal straw, see E. Hauser and A. Haug, Zts. ang. Chem. 1918, **31**, 99; abst. C. A. 1918, **12**, 2439.

[7] Zts. Schiess. Spreng. 1912, **7**, 257; Wag. Jahr. 1912, I, 438; J. S. C. I. 1912, **31**, 954; C. A. 1913, **7**, 257, 892, 1612.

utilization of nitrocellulose prepared from sulfite cellulose and straw fiber, came to the conclusion that whereas sulfite cellulose appeared to be quite suitable for nitrocellulose manufacture the converse was true with straw. Upon the esterification of straw it was found the nitrocellulose thus produced had a greater solubility in ether alcohol, a lower explosion temperature, and a small yield as compared with the cotton cellulose nitrated under the same conditions. He also made the observation which has repeatedly been corroborated, that morphological structure of the straw presented manufacturing difficulties and was almost impossible to overcome, so that at the present time, products of the nitration of straw do not enter into commercial explosives to an important extent.

Nitrated Corn Pith. In 1889 the Marsden Company of New Jersey[1] obtained patent protection for a material claimed as suitable for the manufacture of dynamite, wherein raw pith of maize or corn stalk was nitrated, but they found that the sap and other matters contained in the cells and adherent to the natural pith resulted in a violent reaction with an increase of temperature, partial destruction of the cellular structure, imperfect nitration of the residue, and in endeavoring to use this nitrated product in the production of chemical compounds, this nitrated material contaminated the product to an undesirable extent. In some cases it was found the interior portions of the pith were not reached or affected by the acid and attempts to remove the deleterious material or the acids used in nitrating by means of washing and drying, proved ineffective in their hands. They, however, found it possible to eliminate these objectionable characteristics and uniformly nitrate the pith so as to produce a commercially valuable article therefrom by first separating the latter from the woody shell or outer fibrous portion of the stalk, then comminuting the pith until the particles are about the size of grains of rice; finally drying the latter by a blast or current of heated air, as a preliminary to immersing in the nitrate bath. L. Nottelle and L. Leroux[2] have described combinations of nitrated pith (their so-called "nitro-epidermose") with nitrocellulose using as a typical nitrating bath one containing but two per cent.

[1] E. P. 6656, 1899; J. S. C. I. 1899, **18**, 756.

[2] F. P. 347702, 1904; abst. Mon. Sci. 1906, **65**, 143.

of nitric acid, one-half per cent. sulfuric acid and two per cent. of zinc chloride by weight; this nitration (?) (according to the claims of the patentee) imparting distinct commercial advantages to the product so treated. The International Smokeless Powder and Dynamite Co.,[1] in order to obtain a powder with a higher content of nitrogen of greater ballistic power, and also increasing the percentage of soluble nitrocellulose thus securing a better colloid, combined nitrated Indian corn or maize with other nitrocellulose. In their preferred method, 100 pounds of the pure dried cellulose is treated with approximately 2,000 lbs. or more of mixed acids of the approximate strength of from 56 to 57 per cent. by weight of sulfuric acid, and from 20 to 29 per cent. of nitric acid so that the resulting mixture titrates approximately a minimum acidity of 85%. The period of nitration varies from 18 to 33 minutes according to the strength of the acid and the temperature, the bath being meanwhile maintained during nitration at about 35° C., although the statement of the patentees is to the effect that a slight variation from the temperature does not injuriously affect the nitration of the material. After the cellulose has remained in the mixture for the desired length of time it is claimed nitration progresses to a degree showing approximately 13.10 per cent. of nitrogen, at which point the nitrated product has assumed a physical and chemical state which admits of colloiding at least 95 per cent. of it by means of the usual mixture of ether in alcohol. The patented process of T. Kelly[2] for the nitration of leaves or plants, especially of those of the Australian Eucalypti and the Australian Melaleucæ; and the method of C. Hengst[3] for the nitration of Esparto fiber, have not so far as the author is aware been placed upon a manufacturing basis.

In 1878, W. Eales[4] obtained patent protection for the manufacture of a fuse of nitrated flax or hemp impregnated with saltpeter or salts of chloric, chromic or picric acids.

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[1] E. P. 23252, 1900; J. S. C. I. 1901, **20**, 388.

[2] E. P. 8680, 1899; J. S. C. I. 1899, **18**, 1155; Mon. Sci. 1901, **57**, 148. For the nitration of green eucalyptus leaves, see T. Kelly, E. P. 8679, 1899; J. S. C. I. 1899, **18**, 858; Mon. Sci. 1901, **57**, 148.

[3] E. P. 18002, 1898; J. S. C. I. 1899, **18**, 787; Mon. Sci. 1900, **56**, 131.

[4] D. R. P. 1853, 1878; Dingl. Poly. 1878, **230**, 188; Chem. Ind. 1878, **1**, 275; Wag. Jahr. 1878, **24**, 466. W. Hancock and O. Dahl (Chem. News, 1895, **72**, 16. J. C. S. 1895, **68**, i, 493; J. S. C. I. 1895, **14**, 897; Ber. 1895, **28**, 1558) have reported that the pith like stem of Aeschynomene Aspera gave low yields of nitrate (110%). The nitrates also contained a low proportion of O.NO_2 groups, yielding on analysis 7-9% N. The nitrated product was found to be insoluble in the usual nitrocellulose solvents.

Nitrojute. The explosive bodies formed by the nitration of such lignocelluloses as jute, have been investigated by C. Cross and E. Bevan,[1] by O. Mühlhäuser, and by H. Lifschütz. The former chemists nitrated jute with a mixture of equal volumes of nitric acid (sp. gr. 1.43) and sulfuric acid (sp. gr. 1.8) at a temperature of 18° and found that the maximum of nitration occurred at the end of 15 minutes, the yield on one hundred parts of original jute fiber being 146 parts by weight. The maximum nitration was 154.4 parts. The reaction occurs according to the equation:

$$C_{12}H_{18}O_9 + 3HNO_3 = C_{12}H_{15}O_6(NO_3)_3 + 3H_2O$$

This is equivalent to a gain in weight of 44%, while the conversion into tetranitrate is 58%; the formation of the latter however, appears to be the limit of nitration of jute fiber, and if we represent the lignocellulose molecule by a C_{12} formula, 4 alcoholic hydroxyl groups are indicated. The limit of nitrogen obtained was 11.5%.

O. Mühlhäuser[2] has investigated the value of jute as a raw material for guncotton manufacture. According to his process jute purified with caustic soda is preferably treated with 15 parts of nitric-sulfuric acid mixture consisting of one part nitric acid of 1.52 sp. gr. and 2 parts sulfuric acid 1.84 sp. gr. The product is obtained as a light brown powder, consisting in the main of pentanitrocellulose, insoluble in water, ether, benzene or alcohol, partially (11.93%) soluble in ether-alcohol, and dissolving completely in ethyl acetate and nitrobenzene. The explosive effect is stated to be similar to nitrocotton. The product is readily decomposed by dilute solutions of alkalis and alkali carbonates, but not sufficiently so that the nitro groups are split off. With varying proportions of nitric and sulfuric acids the following results were obtained:

[1] J. C. S. 1889, **55**, 199; abst. Proc. U. S. Naval Inst. 1889, **15**, 311; Chem. News, 1889, **60**, 13; Chem. Centr. 1889, **60**, II, 283; Jahr. Chem. 1889, **42**, 612; Wag. Jahr. 1889, **35**, 1130.

[2] Chem. Ztg. 1892, **31**, 163; Dingl. Poly. 1892, **283**, 88, 137; Proc. Amer. Pharm. Assoc. 1892, **40**, 1004. Zts. ang. Chem. 1892, **5**, 196; Arms & Explo. 1892–3, **1**, 16; Tech. Chem. Jahr. 1891, **14**, 136; Apoth. Ztg. 1892, 86; J. S. C. I. 1892, **11**, 546, 937; Jahr. Chem. 1892, **45**, 2734; Chem. Tech. Rep. 1892, **31**, I, 224; Wag. Jahr. 1892, **38**, 373; Ber. 1892, **25**, 153-R; Bull. Soc. Chim. 1892, **39**, 444. Will states the hygroscopicity of nitrojute (10.28% N) as 4.44% as against 10.8% for the original jute; and nitrated hemp as 1.78% (for 12.8% N) and 1.91% (12.52% N).

Experiment	HNO_3		H_2SO_4	Yield	Ignition Point	N
I	1	:	–	129.5%	170° C.	11.96%
II	1	:	2	132.2%	167° C.	12.15%
III	1	:	3	135.8%	169° C.	11.91%

C. Cross and E. Bevan[1] in reinvestigating this subject, have contributed additional data.

H. Lifschütz has studied the action of nitric and sulfuric acid on vegetable fibers such as jute, hemp, wood shavings and straw and has found that certain mixtures of diluted nitric and sulfuric acids containing 32% sulfuric and 18% to 20% of nitric acid, in the cold or at temperatures of 45 to 50 degrees readily oxidize the impurities of cellulose, or convert them into a soluble form without nitration, but with the development of gas.[2]

Nitrojute has been used in the composition of several smokeless powders especially the Cooppal Smokeless Powder, although the general consensus of opinion is that there is no obvious advantage in the use of lignified textile fibers as raw material for explosive nitrates. Theoretically the trinitrate of jute corresponds to 9.5% nitrogen and the tetranitrate to 11.5%. When used in smokeless powder nitrojute gives a bulky product, easy firing with quick combustion and even penetration. There is a decided tendency however toward decomposition, and considerable washing is required in order to obtain a stable nitrated product. For this reason nitrojute, as yet, has not become an important factor in smokeless powder manufacture.

Nitrolignin. In the early days of cellulose ester history, the nitration of wood received attention, as evidenced by the researches of L. Svanberg,[3] C. Mosander,[4] and B. Wrede,[5] published in 1846. It was E. Schultze however who by his smokeless powder patented in 1864,[6] in which nitrated wood fiber impregnated with oxygen-carrying salts and carrying potassium nitrate, and modified in 1868[1] by the addition of nitroglycerol, may be said to have laid the foundation for the modern bulk sporting powders. "Schultze Gunpowder," and "Schultze White Cannon Powder" was for many years made in large quantities in England and on the Continent. Acapnia and Cooppal Powder were similar.

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[1] J. S. C. I. 1892, **11**, 214; abst. J. C. S. 1893, **64**, i, 295; Jahr. Chem. 1893, **46**, 2735.

[2] H. Lifschütz, Ber. 1891, **24**, 1186; abst. Jahr. Chem. 1891, 2811; J. C. S. 1891, **60**, 814; Chem. Centr. 1891, **62**, I, 1055.

[3] Oefvers. af K. Vet. Acad. Förhandl. **3**, 322; abst. Berz. Jahr. 1848, **27**, 416.

[4] Oefvers. af K. Vet. Acad. Förhandl. **3**, 290; abst. Berz. Jahr. 1848, **27**, 416.

[5] Oefvers. af K. Vet. Acad. Förhandl. **3**, 291; abst. Berz. Jahr. 1848, **27**, 416.

[6] E. P. 900, 1864. Deut. Ind. Ztg. 1865, 96; Schweiz. Poly. Zts. 1865, 52; Dingl. Poly. 1865, **175**, 453; Berg. u. Hüttenm. Ztg. 1865, 271; Poly. Centr. 1865, **31**, 555; Poly. Notiz. 1865, **20**, 126; Chem. Centr. 1865, **36**, 703; Wag. Jahr. 1864, **10**, 251; 1865, **11**, 313; Jahr. Chem. 1865, **18**, 784;

The work of Schultze was followed by that of J. Muschamp,[2] F. Abel and E. Brown,[3] G. Clark,[4] Trütschler-Falkenstein,[5] H.

Wieck's Ill. Deut. Gewerbeztg. 1865, No. 2; Elsner Chem. Tech. Mitt. 1864–5, **14,** 177. "Das neue Chemiche Schiesspulver, Berlin, 1865, 35; abst. Wag. Jahr. 1864, **10,** 245; Dingl. Poly. 1864, **174,** 323; 1865, **176,** 165; Berg. u. Huttenm. Ztg. 1864, 348; Mon. Sci. 1865, **7,** 1059; Chem. News, 1865, **12,** 182. Oest. Milit. Ztg. 1866, **2,** 291; abst. Berg. u. Hüttenm. Ztg. 1864, 236. Allgem. Milit. Ztg No. 12; abst. Rev. d'Artil. 1885, **26,** 188; 1886, **29,** 530; 1887, **30,** 308. D. R. P. 38363, 1886; abst Dingl. Poly. 1887, **265,** 274. U. S. P. 359289, 1887; abst. J. A. C. S. 1887, **9,** 78. Stroblberger, Dingl. Poly 1869, **192,** 73; Poly. Centr. 1869, **35,** 517; Gewerbebl Würtemberg, 1869, 251; Deut. Ind. Ztg. 1869, 78; Wieck's Ill. Deut Gewerbeztg. 1869, 94. Les Mondes, 1865, **9,** 451. Baendisch powder is a variety of Schultze powder. Collodin, or Boltmann's collodin, also called Nitroxylin (Brokhaus Konversations Lexicon, 1901, **4,** 370) is an explosive similar to Schultze powder. The properties claimed for the Schultze powder are, that it gives less pressure on the powder chamber than ordinary powder; that it is smokeless, its explosion gases being very light; that, weight for weight, it has more than twice the propelling power of black powder, and that it leaves less residue in the gun barrel.

[1] E. P. 2542, 1868. Schultze made his powder from well purified and partly nitrated wood. For this purpose he sawed the wood into sheets about $^1/_{16}$ inch thick, which were passed through a machine that punched out discs or grains of uniform size. The grains were then deprived of their resinous matter by being boiled in sodium carbonate solution, washed, steamed, and then bleached with calcium hypochlorite solution, finally washing and drying. The lignocellulose thus obtained was nitrated in a mixture of nitric and sulfuric acids similar to that used for nitrocotton formation. The nitrated material was then steeped in a solution of potassium and barium nitrates, and when dry the powder was finished

[2] E. P. 1326, 1871; abst. Ber. 1872, **4,** 122; Poly. Centr. 1872, **38,** 396; Chem. Tech. Mitth. 1871–72, 60; Deut. Ind. Ztg. 1872, 128; Wag. Jahr. 1872, **18,** 297. F. P. 94461, 1872; abst. Bull. Soc. Chim. 1873, **21,** 334; Mon. Sci. 1873, **15,** 835; Ber. 1873, **6,** 1138; Wag. Jahr. 1873, **19,** 331. U. S. P. 128450, 1872. See also J. Muschamp, E. P. 3293, 1866. He first disintegrated the wood by means of a clipping machine, which was then boiled with caustic soda for 6 hours at a pressure of from 100 to 200 lbs. per sq. in., and after washing free from alkali, was dried at a low heat. The wood was nitrated in a bath of 1 part HNO_3 of sp. gr. 1.50, and 2 parts (by vol.) H_2SO_4 sp. gr. 1.80–1.84. After immersion 24–30 hours in the cooled nitrating bath, the acid was removed by washing and poaching, aided by the addition of small amounts of sodium carbonate.

[3] E. P. 3115, 1868; abst. Deut. Industrieztg. 1868, 485; Chem. Tech. Rep. 1868, **7,** II, 149.

[4] E. P. 1210, 1868. A. Jaksch (Chem. Ztg. 1890, **14,** 303; abst. Jahr. Chem. 1890, 2709) has reported on the examination of an English smoke-

Mayhofer,[1] J. Anders,[2] H. Gruson and A. Hellhoff,[3] W. Wolff and M. v. Förster,[4] C. Dixon,[5] Lafaye,[6] and Zellstoff-fabrik Waldhof,[7] the Meganite of Schückher & Co.,[8] all of which contained the nitrated lignocelluloses as the essential base. The Lithotrite of Antheunis,[9] the Woodnite of Chabert,[10] and the Silotwor of W. v. Ruckterschell,[11] as well as the explosive combinations known as Oriasite, Krummel Dynamite, Miner's Friend Powder, Patent Gunpowder, Petralite,[12] Rifleite,[13] Xylobrome, Smokeless Blasting Powder, Bautzen Powder, and the Vigorite of the Hamilton Powder Co., all belong to this category, and represent more or less successful attempts at the commercial

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less sporting powder composed of lignonitrocellulose and containing 4% barium nitrate, of which he obtained a similar product by stirring thoroughly purified lignin into a cooled mixture of 1 part fuming nitric acid and 2 parts concentrated sulfuric acid until a thick paste results. After 6 hours action the mass is thoroughly washed with water, then boiled for 15 min. in a strong barium nitrate solution, pressed and dried.

[5] Deut. Indztg. 1875, 375; abst. Wag. Jahr. 1875, **21**, 532; Poly. Centr. 1875, **41**, 1362; Chem. Tech. Rep. 1875, **14**, I, 217. "Smokeless blasting powder" gave on analysis, nitrolignin 23.84%, aromatic nitrocompounds (dinitrobenzene, dinitrotoluene, nitrobenzene, nitronaphthalene) 50.3%, barium and potassium nitrates, 25.48%, moisture 0.38%. The Lignite of Ballabene (J. S. C I. 1885, **4**, 366) is claimed to consist of nitrolignin 20%–15%, nitroglycerol 80%–85%.

[1] E. P. 1563, 1878; abst. Wag. Jahr. 1878, **24**, 466; Chem. Ind. 1878, **1**, 214.

[2] E. P. 800, 801, 1881; abst. J. A. C. S. 1882, **4**, 48; Wag. Jahr. 1881, **27**, 331; Chem. Ind. 1881, **4**, 140, 384; Ber. 1881, **14**, 2318; Jahr. rein Chem. 1881, **9**, 136; Chem. Tech. Rep. 1881, **20**, II, 136; J. A. C. S. 1882, **4**, 48.

[3] E. P. 2836, 1882; abst. J. S. C. I. 1882, **1**, 247, 282; 1883, **2**, 296.

[4] E. P. 3866, 1883; 13522, 1884; abst. J. S. C. I. 1885, **4**, 243. See also Mon. Sci. 1911, **74**, 156.

[5] E. P. 2991, 1885; abst. J. S. C. I. 1885, **4**, 247. Lannoy's White powder, made in Belgium, resembles Schultze's powder, and consists of nitrated wood or bran with sulfur and $NaNO_3$. It is said to be a variety of Lithofracteur. The claim for this powder is that it renders rock without great shattering, and hence with but few flying fragments. It is difficult of ignition, and hence burns slowly. It is costly, "and leaves on explosion a strong and stinking smoke."

[6] F. P. 192369, 1888; abst. Mon. Sci. 1889, **33**, 633.

For the composition of American Wood Powder, grade "C," "E," "Ten bore trap," "Twelve bore trap," see Arms and Explos. 1893, **2**, 30.

[7] E. P. 336, 1891; abst. J. S. C. I. 1892, **11**, 180; Mon. Sci. 1892, **40**, 166.

[8] Wag. Jahr. 1888, **34**, 497; Dingl. Poly. 1888, **268**, 519.

[9] E. P. 783, 1887; F. P. 166874, 1885; abst. J. S. C. I. 1887, **6**, 160; Mon. Sci. 1885, **27**, 829.

[10] F. P. 191906, 1888; abst. Mon. Sci. 1889, **33**, 507.

[11] E. P. 4349, 1886; F. P. 188560, 1888; abst. J. S. C. I. 1886; **5**, 253, 459; Mon. Sci. 1888, **32**, 1258.

[12] Colliery Guardian, June 22, 1889.

[13] Arms and Explos. 1900, **8**, 19, 21, 50, 69, 82.

exploitation of "fulminating wood" as a satisfactory smokeless powder. The Yellow Powder of Darapsky, was supposed to be modeled after the original Schultze propellants.

Although various improvements were made in uniformity and increase of stability of nitrated lignose by F. Engel,[1] C. Hengst,[2] H. Pipitz,[3] A. de Stubenrauch,[4] K. Edmunds,[5] R. Griffith,[6] O. Schmidt,[7] Springthorpe[8] and C. Clemm, J. Haas and W. Lenz,[9] it is not until comparatively recently that the nitrated lignocelluloses have been prepared in manufacturing quantities answering the stability requirements of modern ballistics. It seems to be very difficult, if not almost impossible to obtain satisfactory and stable nitrocellulose from wood pulp.

In 1887 F. Nettleford investigated the different pyroxylins obtained by the nitration of wood fiber and cotton by the same acid mixture, and found that whereas the former yielded a product with 11.2% N and 41.6% soluble matter, the latter gave the higher degree of nitration and only 8% of soluble matter. His experiments, however, indicated that the nitrated lignose is separable by solvents into different fractions with varying proportions of nitrogen.[10]

In a recently patented process[11] is described the manufacture

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1. E. P 6022, 1887; abst. J. S. C. I 1889, **8**, 818 Wag. Jahr. 1880, **26**, 378; Dingl. Poly. 1886, **261**, 27.
2. E. P. 13656, 1888; abst. J S. C. I. 1889, **8**, 478.
3. E P. 18935, 1898; abst. Chem Ztg 1900, **24**, 41. D R. P 114499, 114500, 1898; abst. J. S. C. I. 1899, **18**, 946; Chem Centr 1900, **71**, II, 1004; Zts. ang Chem. 1900, **13**, 1140, 1141; Jahr. Chem. 1900, **53**, 849; Chem. Ztg 1900, **24**, 933, 954; Mon Sci 1901, **57**, 147, 148; Wag. Jahr. 1900, **46**, I, 395, 396. He (Pipitz, or J. Okell) nitrates alder wood shavings, which are colloided with acetone and alcohol, and then *re-nitrated*.
4. E. P. 2264, 1898; abst. J. S. C. I. 1899, **18**, 400; Arms and Explos. 1899, **7**, 29.
5. E. P. 23416, 1893; abst. J. S. C. I. 1894, **13**, 1090; Mon. Sci. 1895, **46**, 72.
6. E P. 3294, 1877; 11808, 1884; abst. Wag. Jahr. 1886, **32**, 317; Chem. Ind. 1878, **1**, 147, 235; J. S. C. I. 1884, **3**, 497; 1885, **4**, 468, 753.
7. E. P. 116, 1904; abst. Arms and Explos. 1904, **12**, 55; J. S. C. I. 1904, **23**, 385; Chem. Ztg. 1905, **29**, 514.
8. F. P. 207919, 1890; abst. Mon. Sci. 1891, **37**, 400.
9. Can. P. 38004, 1891.
10. Chem. News, 1887, **55**, 241, 306; abst. J. C. S. 1887, **52**, 792; Jahr. Chem. 1887, **40**, 2599; Chem. Tech. Rep. 1887, **26**, 227, 311; Proc. U. S. Naval Inst. 1888, **14**, 161, 162; Wag. Jahr. 1887, **33**, 569. See also E. Baly and J. Chorley, Chem. News, 1895, **71**, 226. C. Cross and E. Bevan, Ber. 1891, **24**, 1772; J. C. S. 1904, **96**, 61.
11. W. Thomson, W. Severn and G. Twycross, U. S. P. 1302455; abst. C. A. 1919, **13**, 1929. E. P. 130665, 1919; abst. J. S. C. I. 1919, **38**, 480-A, 742-A.

of nitrated compounds from the wood of the baobab tree, the fibers of which, microscopically are said to greatly resemble those of cotton. The wood from the center of the tree is considered preferable, although the entire wood can be used. The wood is first mechanically disintegrated by roughly tearing apart the fibers longitudinally, and to a lesser extent transversely, until the fibers are reduced to shreds of about 1–2 mm. thickness. After boiling in dilute caustic soda, followed by treatment with HCl, the fiber becomes separated into substantially individual strands, which are washed free from acid and dried. The latter are then nitrated in the usual manner, forming an ester readily soluble in acetone.

In a study of the relations between the viscosity of cellulose nitrate solutions and the nitration process, with special reference to wood cellulose, G. Leysieffer[1] employed as material a chemically pure wood cellulose prepared from deal. It contained α-cellulose 80.4, β-cellulose 6.8, γ-cellulose 12.8%. The ash amounted to 0.20% and the fat to 0.44%. The nitration with a mixed acid of known composition was performed much in the usual manner; both cold and hot washing were employed. The drying was effected at 36°–40° for twenty-two hours. The nitrogen content of the product was estimated by the Schulze-Tiemann method, and the nitrates were further characterized by solubility determinations in alcohol or ether-alcohol (2:1). The viscosity of the acetone solutions of the nitrates was determined by the Ost viscosimeter.

As the result of a large number of experiments, tables and graphs of which are given in the original article, the following conclusions are drawn: (1) By the nitration of cellulose, the same value for the viscosity is always obtained provided all the factors which influence the internal friction (composition of the nitrating acid, temperature of the bath, duration of the nitration, proportion by weight of cellulose to acid, method of preparation and properties of the cellulose employed) are kept constant. (2) The greater the nitric acid content of a nitrating acid, the higher is the viscosity of the nitrated cellulose in acetone solution. If, however, the percentage content of nitric acid equals or exceeds that of the sulfuric acid, smaller values are found for the internal friction. This diminution is more marked in the case of dilute nitrating acids than of concentrated nitrating acids. Increasing the water content from 0% to about 11% causes an increase of the viscosity, only, however, if the water content exceeds the above limit, smaller values are obtained for the viscosity. (3) Nitration at temperatures below 0° produces esters having high viscosity values. The higher the temperature of nitration, the smaller is the viscosity. (4) The viscosity values vary considerably in the case of nitrates which have been nitrated for only a short time (five to thirty minutes). They increase so long as the nitrogen content increases, but prolonged action of the nitrating acid results in a diminution of the viscosity. (5) A close connection is found between the nitrogen content of a cellulose nitrate and the internal friction of its acetone solution; the higher the nitrogen content, the higher is the viscosity. (6) Acetone solutions of cellulose nitrates become more mobile with keeping, strongly viscous solutions more so than less viscous solutions. (7) The kind, method of preparation, and previous treatment of a cellulose are of great influence on the viscosity. A high content of γ-cellulose causes increased viscosity in the nitrate. Nitrates from cotton cellulose show higher viscosities than those from wood cellulose,

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[1] Koll. Chem. Beihefte, 1918, **10**, 145; abst. J. C. S. 1919, **115**, i, 149; C. A. 1919, **13**, 1529. The Zellstoffabrik Waldhof (Ital. P. 28964, 1891) claim that cellulose from wood by the sulfite process does not give uniform nitrocellulose. Their process consists in comminuting the wood to a very fine powder, pressing into flakes, and nitrating at 71°. This method, it is claimed, results in the formation of a hexanitrocellulose, free from lower nitrates. The smokeless powder of G. Aschan (Swed. P. 11964, 1899; abst. Mon. Sci. 1901, **57**, 287; Chem. Ztg. 1901, **25**, 238; Chem. Tech. Rep. 1901, **40**, 238) consists of nitrated wood, with the addition of bichromates, and permanganates.

C. Schwalbe[1] in giving the German viewpoint on the subject of nitrolignin as a competitor of nitrocellulose, says that whereas up to the present nitrocellulose used in different industries in Germany has almost entirely been prepared from cotton, although wood cellulose in sufficient amount and in a suitable physical condition has been available at a lower price, nevertheless the more expensive cotton is given the preference because pure nitrocellulose is more easily obtained from purified cotton cellulose, and also because the existing impurities in wood cellulose in all

[1] Zts. ang.-Chem. 1914, **27**, I, 662; abst. C. A. 1915, **9**, 715; J. S. C. I. 1915, **34**, 152.

probability exert an influence on the stability and on the process of stabilization.

Recently R. Woodbridge[1] has detailed experiments undertaken on a large scale in the United States in attempts to utilize nitrated wood for military purposes, and has shown that the most important reason why wood cellulose was not used in place of cotton for smokeless powder manufacture was the question of chemical stability of the powder during storage. Inasmuch as comparatively little is known regarding the chemical stability of smokeless powder under practical conditions of long storage, Government officials have naturally been reticent about authorizing supplanting cotton by other forms of cellulose.

Although the du Pont Company had investigated the possibility of the use of nitrated wood powder as the official propellant for the United States government in 1909, due to lack of support from the army and navy heads, the question was temporarily abandoned. However in 1915, when it was announced that Germany was successfully using large amounts of nitrolignin in the place of nitrocotton, extensive large scale experiments were conducted, and as a result, the following generalizations were arrived at:

1. Wood pulp is best nitrated in crepe paper form, although there is a tendency of the paper to gelatinize during nitration, owing to which and to the shortness of the fiber, considerable difficulty is experienced in separating the nitrated cellulose from the nitrating mixture.
2. The yield of nitrocellulose was very low, only 1.2 lbs. per lb. of cellulose, as compared with 1.5 lb. when nitrating cotton.
3. Consumption of acid was high, due to difficulty in wringing the acid from the nitrated product.
4. Considerable difficulty was experienced in the dehydration of the nitrocellulose. Due to the very finely divided condition of the material, it required almost 50% longer to pump the alcohol through, and to remove the excess alcohol.
5. The viscosity of the wood nitrocellulose was much lower than that prepared from cotton, the amount of solvent required for colloiding being about 8% less than when using nitrocotton.
6. Admixture of about 50% linters to wood pulp eliminated

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[1] J. Ind. Eng. Chem. 1920, **12**, 380. Reproduced, Paper, 1920, **26**, 136.

almost entirely the difficulties in manufacture previously mentioned. This mixture gave no difficulties in nitration, the acid recovery was normal, and the yield about 150% by weight, as compared with about 152% for cotton. This indicated a yield of about 1.48 lb. nitrocellulose per pound of sulfite wood cellulose. The pulping of the nitrocellulose was found to require slightly shorter time due to the shorter wood fiber, while the stability was satisfactory.

When made into 3 inch field powder, it was found that the nitrocellulose dehydrated more slowly, required slightly less solvent due to the fact that the viscosity of the nitrocellulose from the wood pulp was lower than the viscosity of the nitrocotton. The general conclusion reached was that the manufacture of nitrocellulose from linters and wood pulp involved no serious difficulties, and gave a product of satisfactory stability and acceptable ballistics.

In the C. Claessen process,[1] dried wood fiber cardboard is either rolled or compressed and the rolls or solid masses thus prepared are distintegrated on a wood working machine. A uniform porous cellulosic material is thus obtained, suitable for nitration in pots or centrifugally.

C. Claessen[2] also mixes wood cellulose and cotton together with water to a thick pulp, which is dried and further mixed. The bleaching may precede or follow the wet mixing. In this way equal parts of the material can be mixed and nitrated together so as to yield a collodion dissolving to a clear liquid and equal in stability to that obtained from nitrocotton.

Nitrated Paper, Pyropaper, Fulminating paper, Dynamogene, has been used in the arts from the earliest days of nitrocellulose development. In 1856 J. Joyce[3] employed nitrated paper in percussion caps to cover the usual explosive mixture. Three years later appeared the process of A. Church[4] for the impregnation of nitrated paper with the salts of metals which give off a decided spectrum, for use in fireworks. The processes of Darapsky,[5] G. Melland,[6] and E. Liesegang[1] are along similar lines. It was early recognized that nitrated paper gave a readily flowable and colorless collodion especially suitable for photographic purposes, and the methods of J. Bienert,[2] and B. Schratzenthaller[3] are based on this observation.

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[1] D. R. P. 300069, 1915; abst. Chem. Zentr. 1920, **91**, II 350.

[2] D. R. P. 300844, 1915; abst. J. S. C. I. 1920, **39**, 315-A.

[3] Le Technologist, 1856, 603; abst. Poly. Centr. 1856, **22**, 1469.

[4] Chem. News, 1859, **1**, 36; abst. Poly. Centr. 1860, **26**, 924; Zts. Chem. 1860, **3**, No. 4.

[5] Dingl. Poly. 1865, **175**, 451; 1866, **181**, 150; abst. Jahr. Chem. 1865, **18**, 784; Mechanics Mag. 1866, 227; Poly. Notizbl. 1866, **21**, 223;

C. Ditmar[4] and S. Emmens nitrated paper and steeped the product in picric acid and other solutions in the formation of explosive combinations.[5] The smokeless powder of the Explosivstoff-Werke Spiralit Ges.,[6] and the "lightning paper" of A. Brock[7] used in toy fireworks balloons all employed nitropaper.

The major portion of the celluloids and other pyroxylin plastics made throughout the world at the present time use exclusively nitropaper as the inflammable cellulose ester. Grass bleached tissue paper in small strips, after drying to a predetermined moisture content is nitrated mechanically as described in detail in the succeeding chapter. There is no question but what the finest pyroxylin lacquers are to be obtained from the nitration of properly prepared tissue paper rather than from cotton, and the same is true of celluloid intended for transparent sheets and for the formation of artificial ivory. In ready solubility, ease of nitration, nearness in approach to colorless when dissolved, and ready solution in solvent combinations, tissue paper is preferable to cotton.

Nitrated Starch (Nitroamylin, Nitrostarch). Since 1833, when H. Braconnot produced "Xyloidine" by the action of nitric acid upon starch in the presence of sulfuric acid, numerous attempts have been made to prepare nitrated starch in a pure and

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Poly. Centr. 1866, **32**, 1146; Gewerbebl. Kurhessen, 1866, 866; Wag. Jahr. 1866, **12**, 296.

[6] Mechan. Mag. April. 1866; abst. Dingl. Poly. 1866, **181**, 150; Jahr. Chem. 1866, **19**, 859. Deut. Ind. Ztg. 1866, 175; Chem. Tech. Rep. 1866, **5**, I, 101; Cosmos, 1866, 101; Chem. Tech. Mitth. 1866–7, 249; Poly. Notizbl. 1866, **21**, 222.

[1] Poly. Notiz. 1866, **21**, No. 18; Photo. Archiv. 1866, 281; Poly. Centr. 1866, **32**, 1564; Dingl. Poly. 1866, **182**, 151; Elsner. Mitth. 1866–67, 31; Col. Cour. Feb. 26, 1870.

[2] Pharm. Zts. Russ. 1880, 708; **22**, 4; abst. Chem. Ind. 1881, **4**, 129; Jahr. Chem. 1883, **36**, 1779.

[3] E. P. 3976, 1898; abst. Arms and Explos. 1898, **6**, 139; J. S. C. I. 1898, **17**, 489.

[4] U. S. P. 145403, 1873; abst. Amer. Chemist, 1874, **4**, 319.

[5] E. P. 3852, 1890; abst. J. S. C. I. 1891, **10**, 484.

[6] E. P. 8250, 1898.

[7] E. P. 22988, 1900.

stable state, primarily for explosive purposes but also for the replacement of the nitrocelluloses in the peaceful arts. Until comparatively recently, however, it has been found impossible to nitrate starch on a manufacturing scale as a direct competitor of nitrated cellulose, due apparently to the extensive washing required to eliminate traces of acid, and also to the deficient stability which the finished product invariably has shown. Irrespective of the cheapness and abundance of the raw material, starch has, up to the present time, been unable to effectually displace cotton for nitrating purposes to any great extent. The physical difficulties, due to the morphological structure of the starch wherein upon nitration the exterior is nitrated whereas the interior of the starch granule is but incompletely or imperfectly esterified, and the difficulty of subsequent purification, have in general proven insurmountable barriers to the extensive replacement of nitrostarch in the warlike and peaceful arts.

The investigations of H. Braconnot[1] and subsequent workers J. Pelouze,[2] J. Liebig,[3] C. Buijs-Ballot,[4] C. Gerhard, A. Bechamp,[5] J. deVry,[6] and E. Reichardt[7] were more in the nature of academic investigations and had little to do with the question of preparing nitrated starch of acceptable stability, as this term is understood in modern ballistics, especially from a practical point of view.

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[1] Ann. Chim. Phys. 1833, **52,** 290; abst. Berz. Jahr. 1835, **14,** 325; 1840, **19,** 437; Pogg. Ann. 1833, **29,** 176; Ann. 1833, **7,** 245; Schw. J. **68,** 368. C. Blondeau (Ann. Chim. Phys. 1863, (3), **68,** 462; abst. Jahr. Chem. 1863, **16,** 567) divided the nitrated carbohydrates into Fulminose (nitrocellulose) and Fulminam (nitrated starch).

[2] Ann. 1839, **29,** 38; Compt. rend. 1838, **7,** 713; **23,** 893. J. prakt. Chem. 1839, **16,** 168.

[3] Ann. 1833, **5,** 285; abst. J. Pharm. Chim. 1833, **19,** 612.

[4] Scheik. Onderzoek, Utrecht, 1842, No. 3; abst. J. prakt. Chem. 1844, **31,** 309; Ann. 1843, **45,** 47; Berz. Jahr. 1844, **23,** 385.

[5] Compt. rend. 1853, **37,** 134; abst. Instit. 1853, 261; J. prakt. Chem. 1853, **60,** 187; Chem. Centr. 1853, **24,** 703; Jahr. Chem. 1853, **7,** 550. Ann. Chim. Phys. 1862, **64,** 311, 322; abst. Chem. Centr. 1862, **33,** 865; Wag. Jahr. 1862, **8,** 280; Jahr. Chem. 1862, **15,** 469; Rep. Chim. Pure, 1862, **4,** 358.

[6] Compt. rend. 1841, **12,** 120; Watts. Dict. Chem. 1877, **5,** 410. Compt. rend. 1847, **24,** 19; abst. Jahr. Chem. 1847–48, **1,** 1139. J. prakt. Chem. 1847, **40,** 420.

[7] Ber. 1875, **8,** 1020; abst. Jahr. Chem. 1875, **28,** 787. See C. Reichen, E. P. 2266, 1865. E. I. du Pont de Nemours Co. (E. P. 22623, 1912; abst. J. S. C. I. 1913, **32,** 1105) make pyroxylin plastics by combining nitrostarch and acetaldol. This latter, which is a liquid, polymerizes into a solid at ordinary temperatures and the polymerized product is reconverted into liquid acetaldol on heating. The blasting explosive of G. Peters (U. S. P. 1048578, 1912; abst. J. S. C. I. 1913, **7,** 703; Mon. Sci. 1913, **79,** 148) comprises ammonium nitrate 75%, nitrated potato starch 20%, and 5 parts of an 80% solution of nitrobenzene in asphalt.

"The White Powder" or "White Gunpowder" developed in 1861 by the Austrian engineer F. von Uchatius,[1] was prepared by dissolving one part by weight of potato starch in eight parts of fuming nitric acid, care being taken to keep the nitrating mixture cool. The thick fluid obtained was poured in a thin stream into 16 parts of concentrated sulfuric acid with constant agitation, the resulting jelly allowed to remain at rest for 12 hours and then repeatedly washed, alternately with pure water and with a dilute soda solution. The white powder finally obtained was then dried by heat not exceeding 50° to 60° C. but was so strongly hygroscopic and powerful in its detonating properties as to render its effect for use in fire arms dubious, according to the report of the Austrian Commission appointed to investigate this product.

The next year[2] appeared the patented processes of T. and S. Davey in which starch was treated with nitric or nitric and sulfuric acids, preferably in the proportion of one of nitric acid to three of sulfuric acid, the mixture being boiled with as much starch as will pass into solution, excess of water and acids being separated by dialysis. The neutralized product obtained was then mixed with gunpowder materials in the proportion of 4 to 6 per cent. of nitrated starch.

C. Dittmar,[3] in experiments which resulted in his placing upon the market the explosive "Dualin," employed nitrostarch and nitromannite in combination with nitrocellulose and nitroglycerol in different proportions according to the strength of the finished explosive desired.

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[1] Dingl. Poly. 1854, **132**, 371; Ber. Wien. Akad. Wissensch. **10**, 748. Dingl. Poly. 1861, **161**, 146; abst. Poly. Centr. 1861, **27**, 1367; Poly. Notizbl. 1861, **16**, 309; Wag. Jahr. 1861, **7**, 234. For further experiments upon the product of Uchatius see Sauerwein, Dingl Poly. 1862, **164**, 123; abst. Proc. Amer. Pharm. Assoc. 1862, **11**, 144; Dingl. Poly. 1862, **166**, 123; abst. Jahr. Chem. 1862, **15**, 665; Poly. Centr. 1862, **28**, 459; Wag. Jahr. 1861, **7**, 234; 1862, **8**, 280; Chem. Centr. 1862, **33**, 865; Bayer Kunst. u. Gewerbebl. 1862, 189; Chem. Tech. Mitth. 1861-2, 117.

[2] E. P. 2072, 1862; 2832, 1877; abst. Chem. Centr. 1878, **49**, 640; Ber. 1878, **11**, 1390; Wag. Jahr. 1878, **23**, 467; Dingl. Poly. 1877, **230**, 188; Chem. Ind. 1878, **1**, 108; F. P. 126339, 1879; abst. Mon. Sci. 1879, **21**, 1037. See also Chem. News, 1906, **93**, 106. In the H. Maxim process (E. P. 18682, 1894; abst. J. S. C. I. 1894, **13**, 1219), is described a fulminating composition suitable for detonating high explosives made from nitroglycerol thickened with pyroxylin or nitrostarch, with the addition of mercuric fulminate, nitrobenzene being added as a deterrant. The G. Lezinsky process (E. P. 22555, 1908; abst. J. S. C. I. 1909, **28**, 817) comprizes an explosive of nitrated resin and wheat starch with potassium chlorate.

[3] Amer. Artiz. 1870, **6**, 90; Dingl. Poly. 1870, **196**, 89; Chem. Centr. 1870, **41**, 366; Poly. Centr. 1870, **36**, 930; Deut. Ind. Ztg. 1870, **115**, 372; 1869, 346; Zts. Oest. Ing. Vereins, 1870, 254; Wag. Jahr. 1870, **16**, 218; 1871, **17**, 217; Chem. Tech. Mitth. 1869-70, 38; Breslauer Gewerbebl. 1869, 73;

T. Hess and J. Schwab,[1] in endeavoring to determine the cause of the instability of the nitrated starches which had been prepared up to that time, treated the decomposition products of nitrostarch and nitromannite with alcoholic potash and similar reducing agents.

J. Engels[2] endeavored to modify the disruptive effect of nitrostarch by combining the same with nitromannite, nitrated paper and nitroglycerol in the presence of an alkaline body as waterglass, his product known commercially as Atlas Dynamite comprizing pyroxylin 18 to 28 parts, nitroglycerol 55 to 44, pyropaper 5 to 10, nitrostarch 20 to 16, with one part each of nitromannite and waterglass. It was found that the addition of small amounts of alkali, while it retarded decomposition, did not prevent the changing of the powder upon storage to a brown friable mass.

The explosive of E. Luck and F. Roberts[3] was somewhat similar.

C. Noroy[4] patented in 1888 the use of nitrostarch in combination with metallic oxides as an improved material for dyeing, claiming that nitrated starch prepared by the process disclosed in his patent application, possesses the property of dissolving small amounts of nearly all the known metallic and earthy oxides,

Deut. Bauztg. 1869, 364; Berggeist, 1869, 246; Chem. Tech. Rep. 1869, **8**, II, 97; 1870, **9**, II, 102; Bull. Soc. Chim. 1870, **14**, 349; Jahr. Chem. 1870, **23**, 1128; Amer. Chemist, 1870, **1**, 79; Ber. 1869, **2**, 256. See W. Syniewsky, Ber. 1898, **31**, 1795.

[1] Wien. Acad. Ber. 1877, **75**, II, 702; abst. Jahr. Chem. 1877, **30**, 524; J. C. S. 1878, **34**, 130; Dingl. Poly. 1877, **225**, 611; Wag. Jahr. 1877, **23**, 395.

[2] D. R. P. 10232, 1879; abst. Chem Ztg. 1880, **4**, 522, 733; Wag. Jahr. 1880, **26**, 377; 1886, **32**, 319; 1887, **33**, 575; Jahr. Chem. 1888, **41**, 1311; Dingl. Poly. 1880, **238**, 328, 332; Chem. Ind. 1880, **3**, 276, Chem Tech. Rep. 1880, **19**, I, 339; Industrieblätter, 1880, 339; J. A. C. S. 1880, **2**, 406.

[3] E. P. 12292, 1884; abst. Wag. Jahr. 1885, **31**, 279; J. S. C. I. 1884, **3**, 498; 1885, **4**, 300, 418; Chem. Tech. Rep. 1890, **29**, I, 33.

[4] E. P. 17094, 1888; abst. J. S. C. I. 1889, **8**, 878; J. Soc. Dyers Col. 1888, **4**, 169. The Satanite Powder Co. (E. P. 7719, 1911; abst. C. A. 1912, **6**, 2843; J. S. C. I. 1911, **31**, 650. U. S. P. 989519, 1911; abst. J. S. C. I. 1911, **31**, 1186) have described an explosive composed of resin and starch nitrated together. Mon. Sci. 1912, **77**, 31; Zts. Schiess. Spreng. 1911, **6**, 377; Chem. Ztg. Rep. 1912, **36**, 531.

such as those of iron, copper, zinc, chromium, nickel, antimony, tin, arsenic, calcium and aluminium, and of preventing them from being reprecipitated by the addition of an excess of the alkaline oxides or carbonates. It is this property which enables the patentee to effect the dyeing in a more or less alkaline medium in which cotton and wool and, in general, all animal and vegetable and textile materials can be properly dyed.

The combination of nitrostarch and nitroglycerol as advocated by C. Volney[1] was never able to seriously compete with the analogous nitroglycerol-nitrocellulose combinations as typified by cordite.

J. Sargent[2] sought to increase the stability and render more uniform the esterification of the starch granule by a reduction in temperature in the nitrating process. He appreciated the fact that—as in the nitrating of cotton—it is necessary for the attainment of uniform results that the esterified cellulose be practically anhydrous before subjection to nitration. To that end he dried the starch in closed containers at a temperature of 100°–140° and cooled to below 4° before immersing in the bath of one volume of nitric acid, of 1.5 sp. gr. and two volumes of sulfuric acid 1.84 sp. gr." The mixture was also cooled to 4° or lower. To each liter of this bath was added 200 grams of starch and the whole thoroughly mixed by constant stirring, the temperature of the combined bath being kept under 6°, by pouring it on to broken ice. This precipitated the nitro compound which settled in a gelatinous mass, which was washed with water and then with dilute alkali and further stabilized by vigorously boiling for ten minutes to remove "those impurities which might interfere with the explosive qualities and impair the stability of the explosive."

W. Schuckher[3] combined stabilization, induration and the introduction of bodies to decrease the inflammability in the preparation of a smokeless powder, and this, perhaps, was the first definite technical attempt to prepare nitrated starch combinations which would be acceptable commercial competitors with the gelatinized nitrocelluloses. He incorporated 50 parts of nitrostarch with potassium, sodium, ammonium, or barium nitrates or picrates, in the presence of nitronaphthalene, or of nitrobenzol or aniline as stabilizer. The nitrostarch was intimately treated with a solvent to the point of incipient gelatinization in order to harden the finished product and increase its density. In the preparation of nitrostarch by the method of Schückher potato starch is dried at a temperature of about 100°

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[1] U. S. P. 366281, 1887; abst. J. A. C. S. 1887, **9**, 158.

[2] E. P. 12316, 1899; abst. J. S. C. I. 1900, **24**, 933. Can. P. 66462, 1900.

[3] E. P. 11665, 1889; abst. J. S. C. I. 1889, **8**, 818. F. P. 199734, 1890; abst. Mon. Sci. 1890, **35**, 331. D. R. P. 51755; abst. Chem. Zentr. 1890, **61**, II, 416; Jahr. Chem. 1890, **43**, 2710; Wag. Jahr. 1890, **36**, 545; Ber. 1890, **23**, 528-R; Tech. Chem. Jahr. 1889, **12**, 157. D. R. P. 54434, 1890; abst. Zts. ang. 1890, **3**, 714; Jahr. Chem. 1890, **43**, 2710; Wag. Jahr. 1890, **36**, 546; Ber. 1891, **24**, 290; Erfind. Erfahr. 1891, **18**, 232. E. P. 4243, 14625, 1890; abst. J. S. C. I. 1891, **10**, 67. F. P. 208248, 1890; abst. Mon. Sci. 1891, **37**, 573.

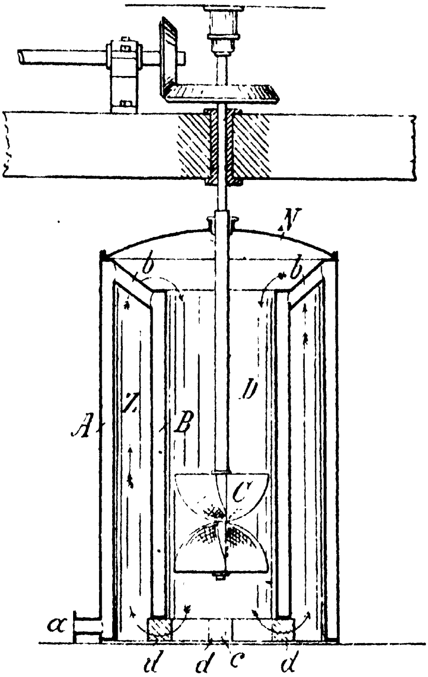

FIG. 143.—THE MÜHLHÄUSER NITROSTARCH MANUFACTURING METHOD

and finely ground, then dissolved at 20°–25° in nitric acid of 1.501 sp. gr., using about ten kilos of acid to each kilo of starch. The solution thus obtained is then mixed with a quantity of mingled sulfuric and nitric acids containing about seventy per cent. sulfuric acid monohydrate and ten per cent. nitric acid monohydrate used in the proportion preferably of about five kilos to each kilo of nitrated starch solution, which is thoroughly agitated with the acid at a temperature of 20°–25°. The nitrated starch is precipitated in a very finely subdivided condition, collected on a filter of guncotton and after filtration freed from residuary acid by pressure in a hydraulic press, the cakes produced being well agitated and thoroughly washed in water. About five parts of soda solution is then added and after remaining

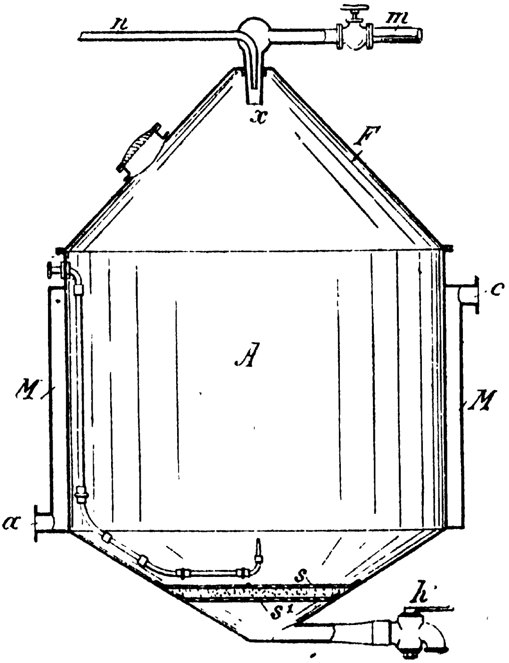

FIG. 144.—MÜHLHÄUSER PROCESS OF NITROSTARCH MANUFACTURE

preparation of a smokeless powder, and this, perhaps, was the first definite technical attempt to prepare nitrated starch combinations which would be acceptable commercial competitors with the gelatinized nitrocelluloses. He incorporated 50 parts of nitrostarch with potassium, sodium, ammonium, or barium nitrates or picrates, in the presence of nitronaphthalene, or of nitrobenzol or aniline as stabilizer. The nitrostarch was intimately treated with a solvent to the point of incipient gelatinization in order to harden the finished product and increase its density. In the preparation of nitrostarch by the method of Schückher potato starch is dried at a temperature of about 100°

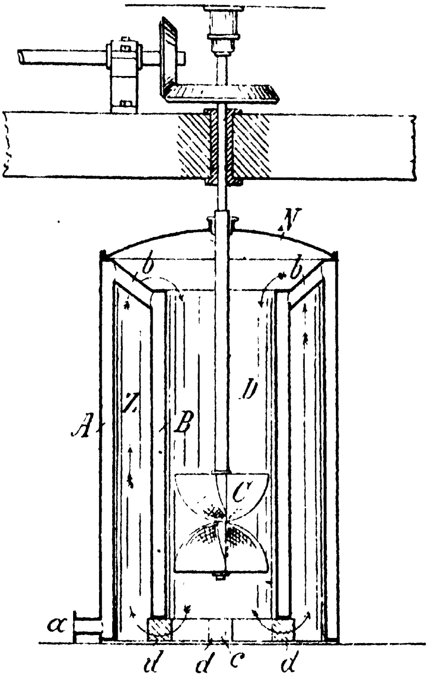

FIG. 143.—THE MÜHLHÄUSER NITROSTARCH MANUFACTURING METHOD

product containing from 10.5 to 10.58 per cent. of nitrogen. Mühlhäuser furnishes the following table relative to the three methods of preparation investigated by him: He was able to prepare and separate two bodies of the following definite composition, viz:

$$\text{(a)}\ C_6H_{7\frac{1}{2}}O_{2\frac{1}{2}}(NO_3)_{72\frac{1}{2}}$$
$$\text{(b)}\ C_6H_7O_4(NO_3)_3$$

or doubling the molecule of starch in order to give the expression whole numbers; and adding a product of 11.1% total nitrogen obtained:

Tetranitrostarch	$C_{12}H_{16}O_6(ONO_2)_4$	nitrogen 11 11%
Pentanitrostarch	$C_{12}H_{15}O_5(ONO_2)_5$	nitrogen 12 75%
Hexanitrostarch	$C_{12}H_{14}O_4(ONO_2)_6$	nitrogen 14 14%

That not nitro compounds but true esters of starch are formed was proven by the fact that the substances separate nitric acid upon treatment with sulfuric acid, while nitric oxide and soluble starch are both regenerated upon treatment with aqueous ferrous chloride. Furthermore, upon shaking a sample with sulfuric acid over mercury, all the N is split off as NO.

In addition to the tetranitrostarch above described Mühlhäuser prepared the penta and hexa derivatives as follows:

Pentanitrostarch. Mühlhäuser obtained, from rice starch and potato starch, by throwing 1 part starch in 30 times its weight of a nitrating acid (1 part HNO_3 to 3-3.5 parts H_2SO_4), a mixture which dissolved in ether-alcohol, and from which, after evaporation of the ether, the pentanitrostarch was obtained as a white granular mass, while tetranitrostarch still remained dissolved in the alcohol. The N content of the former was found to be 12.50%-12.98%.

Hexanitrostarch mixed with pentanitrostarch was obtained by throwing 40 gm. dried starch at ordinary temperature within the course of one-half hour in 400 gm. HNO_3 (1.501) stirring and allowing to stand for half an hour. The solution was then run under stirring in course of one-half hour into 1200 cc. H_2SO_4, 66° Bé., allowed to stand, poured in much water, filtered and worked up as usual. The product gave a N content of 13.22%-13.53%.

The Dynamit Actien-Gesselschaft Nobel[1] replaces nitrobenzol previously advocated by di- or trinitrobenzene, di- or trinitrotoluene, di- or trinitroxylene, mono-, di- or trinitronaphthalene, in conjunction with nitrostarch or nitrodextrin.

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[1] E. P. 5382, 1884; abst. J. S. C. I. 1885, **4**, 417. E. P. 1469, 1888; abst. J. S. C. I. 1888, **7**, 160; 1889, **8**, 78, 133; Proc. U. S. Nav. Inst. 1889,

The patented processes of H. Kolf,[1] A. Pike and W. Thew,[2] and the Explosivstoff-Werke Spiralit Gesellschaft and M. Thorn[3] offer nothing new.

The process of W. Will and F. Lenze[4] for the nitration of starch is to gradually immerse starch under cooling in ten volumes of nitric acid of 1.52 sp. gr., subsequently adding sulfuric acid after about 24 hours. The precipitated nitro product is then well washed with water, extracted with cold and subsequently twice with boiling alcohol, the residue being dissolved in a mixture of alcohol and acetone and the acetone evaporated, whereupon the product remains as a white powder. It is then filtered

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15, 302 E. P 6560, 1888, abst J. S C I. 1888, **7,** 416; 1889, **8,** 238, 420, Proc U S Nav. Inst. 1890, **16,** 46 E P. 6128, 6129, 1891, abst. J. S. C. I. 1892, **11,** 267, 456. F P. 185178, 185179, 185180, abst Mon. Sci 1888, **32,** 756, Tech Chem. Jahr. 1887–8, **10,** 195 F. P 186801; abst. Mon. Sci 1888, **32,** 883. F. P. 212648, 212649, 212650; abst Mon. Sci. 1891, **38,** 1235, 1243; Tech. Chem. Jahr 1891-2, **14,** 142. U. S. P. 456508; abst. J. A. C. S. 1891, **13,** 220; Tech. Chem. Jahr. 1891–2, **14,** 160. D. R. P. 57711; abst Zts ang. Chem. 1891, **4,** 611; Chem Ztg. 1891, **15,** 1474; 1892, **16,** 1279; Chem Tech. Rep. 1891, **30,** II, 255, Wag Jahr. 1891, **37,** 431; Ber. 1892, **25,** 240-R; Meyer Jahr. Chem 1891, **1,** 334; Industriebl. 1891, II, 255; Dingl. Poly. 1892, **284,** 137, Tech. Chem. Jahr. 1891–2, **14,** 144. See also E. P. 1471, 1888, abst. J. S. C. I 1889, **8,** 214; Tech. Chem Jahr. 1890, **12,** 160; Chem Tech. Rep 1890, **29,** I, 224; Zts. ang. Chem. 1889, **2,** 345; Jahr. Chem 1889, **42,** 2682; Wag. Jahr. 1889, **35,** 474. Belg. P. 80419. Ital. P. 22994, 1888.

[1] E. P. 22739, 1892; abst J. S C I. 1893, **12,** 1057. G. Lezinsky, U S P. 762447; abst. Chem. Ztg. 1904, **28,** 648; Chem. Zts. 1904, **3,** 692, Mon. Sci 1905, **63,** 15. U. S. P. 799687; abst J. A. C. S. 1906, **28R,** 230; Mon Sci 1906, **65,** 67, Zts Schiess Spreng. 1906, **1,** 50. D. R. P. 188829; abst Chem. Zentr 1907, **78,** II, 1880, Chem Ztg. Rep. 1907, **31,** 483; Chem Zts. 1907, **6,** 224 F. P 395635; abst Mon Sci. 1910, **73,** 97. E. P. 22555 1908; abst J. S. C. I. 1909, **28,** 817. Swiss P. 45490, 1908, prepares the explosive compound "Hydrox" by combining potassium chlorate, nitrostarch, and nitrated resin.

[2] E P. 26704, 1896; abst. J. S. C. I. 1898, **17,** 69; Chem. Ztg. 1898, **22,** 340; Mon Sci. 1898, **52,** 222; Arms and Explos. 1898, **6,** 66.

[3] E. P. 8250, 1898; D. R. P 102743; abst. Chem. Centr. 1899, **70,** II, 463. The E. Steele process (E. P. 4115, 1906; abst. Zts. Schiess. Spreng. 1907, **2,** 195; J. S. C. I. 1907, **26,** 280; C. A. 1907, **1,** 1489) for rendering explosives practically non-hygroscopic consists in coating the salt (as ammonium nitrate) with nitrated starch and resin, the mass being then atomized with methylated spirit to colloid the nitro compounds, thus rendering the salt impervious, as described in E. P. 14676, 1901; abst. J. S. C. I. 1902, **21,** 1155.

[4] Ber. 1898, **31,** 87; abst. Chem. News, 1898, **77,** 152; J. C. S. 1898, **74,** i, 227; J. S. C. I. 1898, **17,** 271; Bull. Soc. Chim. 1890, **20,** 390; Chem. Centr. 1898, **69,** I, 441; Jahr. Chem. 1898, **51,** 1307; Wag. Jahr. 1898, **44,** 707; Zts. ang. Chem. 1898, **11,** 517.

under suction, boiled with alcohol and washed with water, after which treatment it shows a decomposition point of 194° without previously melting, gave 14.04% nitrogen, was readily soluble in acetone and ethyl acetate and was found perfectly stable after storage for six months at 60°.

The smokeless powder of C. Hengst, patented in 1901,[1] comprized the incorporation of 93% of nitrostarch under runners with 3% potassium nitrate, 1% zinc sulfate and the balance ground charcoal, the composition after drying being mixed with 5% nitroglycerol, 2% linseed oil and 15% acetone.

A. Saposchnikoff[2] has recently investigated nitrostarch obtained by nitration with an acid mixture of nitric acid of sp. gr. 1.51 and sulfuric acid 1.841, which gave 13.44% nitrogen and a molecular weight of 1824–1842, and 1829–1884.

The process of manufacturing nitrostarch as developed by C. Arnold, A. Fox, A. Scott, and H. Roberts,[3] consists in adding the starch to either nitric acid, sulfuric acid, or the waste acid from nitrocellulose manufacture, so as to obtain the precipitation of nitrostarch in the form of a flaky mass which is freed from acid in the usual way by the action of water and afterwards rendered stable by successive boiling with water with or without the addition of small amounts of alkali. The product thus obtained formed the basis of an explosive and celluloid substitute. They claim good results are obtainable by using nitrostarch prepared according to their process (60 to 75 parts with camphor 20 to 30 parts, using waste spirit as the mutual solvent).[1]

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[1] E. P. 15141, 1901; abst. J. S. C. I. 1902, **21,** 1155; Chem. Ztg. 1902, **26,** 1161. D. R. P. 48265; abst. Chem. Centr. 1890, **61,** I, 559; Jahr. Chem. 1889, **42,** 2683, Wag. Jahr 1889, **35,** 662; Ber. 1889, **22,** 525-R; Chem. Tech. Rep. 1890, **29,** I, 222. U. S. P. 640160, 1899.

[2] J. Russ. Phys. Chem. Soc. 1903, **35,** 126; abst. J. C. S. 1903, **84,** i, 402; Bull. Soc. Chim. 1904, **32,** 218; Chem Centr. 1903, **74,** I, 1122; Jahr. Chem. 1903, **56,** 1008; Meyer Jahr. Chem. 1903, **13,** 345.

The explosive of R. Hill (U. S. P. 1334303, 1920; abst. C. A. 1920, **14,** 1609; J S. C. I. 1920, **39,** 386-A) is suitable for blasting and is stated to consist of ammonium perchlorate 45–55%, nitrostarch 35–45% and sodium nitrate or other similar compound which will combine with chlorine produced by the explosion and will thus serve to avoid liberation of chlorine or hydrochloric acid. A small amount of oil, a liquid nitro compound, manganese dioxide and sulfur may also be added.

[3] E. P. 3449, 1906; abst. J. S. C. I. 1907, **26,** 167; C. A. 1907, **1,** 1192; Zts. Schiess. Spreng. 1907, **2,** 177.

In the process of nitrostarch manufacture as disclosed by the Acktienges. Dynamit Nobel (D. R. P. 57711; abst. Mon. Sci. 1892, **40,** 51; Ber. 1892, **25,** 240; Wag. Jahr. 1891, **37,** 431; Zts. ang. Chem. 1891, **4,** 611) dry starch at 100° is treated with HNO_3 of sp. gr. 1.501 at 20°–25°, the starch being substantially dissolved in the acid. It is then precipitated in a large bulk of water, and is stabilized by mixing with a 1% aqueous solution of aniline until thoroughly impregnated, then centrifuged, and finally dried.

G. Bailey[2] nitrates in one operation a mixture of rosin and starch as the basis of an explosive to which he attributes especially desirable properties.

G. Holmes, who has assigned his process to the Eastern Dynamite Co.,[3] stabilizes nitrostarch as prepared by him by boiling it in the presence of an insoluble substance as calcium carbonate capable of neutralizing the acid.[4] Holmes has evidently made a systematic study of the influence of stabilizing bodies upon nitrostarch in a manner similar to the earlier investigations of the influence of stabilizers in conjunction with camphor and nitrocellulose for the preparation of commercial thermoplastic bodies. He has obtained patent protection for the use in connection with starch of ammonium arsenate;[1] ammonium chromate or potassium ammonium chromate;[2] the acetate, propionate, butyrate, stearate and palmitate of ammonia, especially ammonium palmitate,[3] acid ammonium tartrate, sodium ammonium tartrate, neutral ammonium tartrate and potassium ammonium tartrate;[4] the pyro-tartrates such as acid and neutral ammonium pyro-tartrate, sodium ammonium pyro-tartrate and the potassium ammonium compound;[5] mono-, di- and tri-ammonium citrate, sodium ammonium citrate and potassium ammonium citrate;[6] the amides of oxalic acid, as oxamide and oxamic acids;[7] those substituted ureas in which the oxygen is replaced by an inorganic radical such as thiourea and guanidine;[8] an aniline salt as the hydrochloride, nitrate, sulfate, or preferably the oxalate;[9] substituted anilines as chloraniline, bromaniline or preferably nitraniline;[10] the organic aliphatic acid anilids as formanilid, oxanilid and acetanilid;[11] the substituted toluidines including chlortoluidine, bromtoluidine and nitrotoluidine,[12] or the toluidine hydrochlorides, nitrates, sulfates or preferably the oxalates;[13] or the formtoluid, acetoluid or the toluid of oxalic acid;[14] benzamide, dibenzamin and the amid of toluic acid (toluamid).[15] In

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[1] E. P 3450, 1906; abst. J. S. C I 1907, **26,** 274; C A. 1907, **1,** 1147, 1487 A Mikolajczak (F. P. 341911; Mon Sci 1905, **63,** 86; Chem. Ztg. 1904, **28**) a powder containing nitrostarch

[2] U S P. 989519; abst J. S. C. I 1911, **31,** 650, 1186; C. A. 1911, **5,** 2180, Mon. Sci 1912, **77,** 31; Zts. Schiess Spreng 1911, **6,** 377. E P. 7719, 1911; abst C. A 1912, **6,** 2843, J S C I 1911, **30,** 1186; Chem. Ztg. Rep 1912, **36,** 531; Zts. Schiess Spreng 1912, **7,** 81

[3] U. S P 779421, 779422, 1905, abst. J S C. I 1905, **24,** 152; Mon. Sci 1905, **62,** 142, Chem. Ztg 1905, **29,** 105, Chem Zts. 1905, **4,** 113; J. A. C S 1905, **27R,** 541.

[4] Holmes, in describing his process says "The starch is mixed with concentrated nitric and sulfuric acids, preferably in the proportion of 25 parts starch to 100 parts of mixed nitric and sulfuric acids in the following proportion. nitric acid 32.5%, sulfuric acid 64.5%, water 3%, although these limits may be varied somewhat and still produce a satisfactory product. After separation from the acids, the nitrated starch, which is then in an unstable condition due to impurities, is mixed with alcohol and a reagent which has a lower evaporating point than the alcohol, and which reagent alone or in the presence of alcohol, will dissolve the nitrated starch

"As the reagent above mentioned, I have used acetone or ether, both of which have a lower evaporating point than alcohol The acetone alone will dissolve the nitrated starch The ether alone will not dissolve all the nitrated starch, but in conjunction with the alcohol will dissolve substantially all Both acetone and ether have a lower evaporating point than alcohol. Acetone is preferable because a higher nitrated product is obtained than where ether or ether and alcohol is used. With acetone, the lower nitrates remain in the solution, while when ether is used, some of the lower nitrates are subsequently precipitated. Approximately 1 part nitrated starch to 1 part acetone or ether and 2 parts alcohol is preferred. After the nitrated starch has been dissolved, the acetone or ether is evaporated off, leaving the former in suspension in the alcohol. Irrespective of which solvent is used, those impurities which tend to produce instability in the starch will remain in solution in the alcohol while the stable nitrated starch, being insoluble, is precipitated out, and dried, after filtration."

1. U S P 875913, 875914, 1908, abst C A 1908, **2,** 1499, Chem Ztg. Rep. 1908, **32,** 208; Mon Sci 1909, **71,** 127; Zts Schiess. Spreng 1908, **3,** 217.

2. U S P. 875915, 1908; abst C A. 1908, **2,** 1499; Chem Ztg Rep. 1908, **32,** 208; Zts Schiess Spreng 1908, **3,** 217.

3. U. S P. 875916, 1908; abst C. A 1908, **2,** 1499; Chem. Ztg. Rep 1908, **32,** 208; Zts. Schiess Spreng. 1908, **3,** 216.

4. U S. P. 875917, 1908; abst C A 1908, **2,** 1499; Chem Ztg Rep. 1908, **32,** 208; Zts. Schiess Spreng 1908, **3,** 217.

5. U. S P. 875918, 1908; abst C. A 1908, **2,** 1499; Chem Ztg. Rep. 1908, **32,** 208; Zts. Schiess Spreng 1908, **3,** 217

6. U. S. P. 875919, 1908, abst. C A. 1908, **2,** 1499, Chem. Ztg. Rep. 1908, **32,** 208; Zts. Schiess Spreng. 1908, **3,** 217.

7. U. S. P. 875920, 1908, abst C. A. 1908, **2,** 1499, Chem. Ztg. Rep 1908, **32,** 208, Zts. Schiess. Spreng 1908, **3,** 217

8. U. S. P. 875921, 1908, abst C. A 1908, **2,** 1499; Chem. Ztg. Rep. 1908, **32,** 208; Zts Schiess Spreng. 1908, **3,** 217.

9. U. S. P 875923, 1908

10. U. S. P. 875922, 1908.

11. U. S. P. 875924, 1908.

12. U. S. P. 875925, 1908

13. U. S. P. 875926, 1908.

14. U. S. P. 875927, 1908.

15. U S. P. 875928, 1908. In the method of manufacturing nitrostarch explosives as worked out by W. Snelling and W. Laws (U. S. P. 1329211, 1329212, 1920; abst J. S. C. I. 1920, **39,** 249-A) nitrostarch is coated with a heavy mineral oil and then treated with an organic stabilizing agent soluble in the oil. W. Snelling (U. S. P. 1305946, 1919; abst. J. S. C. I. 1920, **39,**

addition to these, patent protection was obtained covering the use of ammonium carbonate[1] and ammonium oxalate.[2]

His preferred explosive,[3] which comprizes a nitrate, carbohydrate, a solid inorganic oxidizing substance, and a non-volatile liquid organic compound is composed of nitrostarch 70, sodium nitrate 25, and nitroglycerol 5.

The nitrolite of C. Lamm[4] and the explosive of the Pulver-Fabrik Hassloch[5] offer nothing new.

In 1911 M. Lindsley[6] assigned to the King Powder Co. a method for the co-nitration of benzene and starch and for an explosive based upon the same,[7] comprizing nitrostarch and nitrosugar each 6.25, nitrobenzene 4, potassium nitrate 52.5, charcoal 10, nitrocellulose 12.5, sulfur 7 and asphalt 1.

The gelatinized propellent explosives containing nitrocompounds such as nitrocellulose, nitromannitol, nitrostarch and nitroglycerol, as developed by F. Nathan, W. Rintoul and T. Baker[8] are rendered more stable by the addition thereto of one

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282-A) has prepared a smokeless powder by mixing nitrostarch with an agent, e. g., liquid trinitrotoluene, which does not gelatinize the nitrostarch during the mixing process, and subsequently heating the mixture to 60°-90° C, to cause "colloidization" The ammonium nitrate explosive of W Snelling (U. S P 1343063, 1920) contains ammonium nitrate in excess of 40% of the entire mixture, nitrostarch and a finely divided material of high covering power interspersed among the particles of the ammonium nitrate

[1] U. S P 895639, 1908, abst. C A 1908, **2,** 3286, Mon. Sci 1909, **71,** 128, Zts Schiess Spreng 1908, **3,** 418 B Flurscheim (U S P. 1343317, 1920; abst C. A 1920, **14,** 2420) has patented cyanamide and calcium cyanide as a nitrostarch stabilizer

[2] U S. P. 891420, 1908, abst C A 1908, **2,** 2995, Chem Ztg. Rep. 1908, **32,** 445; Mon Sci 1909, **71,** 127, Zts Schiess Spreng 1908, **3,** 399

[3] U S P 861177, 1907, abst C A 1907, **1,** 3064, Mon Sci. 1908, **69,** 60, Zts Schiess Spreng 1908, **3,** 18, J S C I 1907, **26,** 991.

[4] His product consisted of nitroglycerol 99-94, nitrocellulose (nitrated cotton, straw or starch) 1-6 Ammonium, sodium or potassium nitrate and light charcoal 50-150 Nitrobenzene is said also to be present It is stated that the above is liable to exudation and is very hygroscopic.

[5] D. R. P. 130523; abst. Jahr. Chem 1902, **55,** 1056; Wag. Jahr. 1902, **48,** I, 363; Zts. ang Chem 1902, **15,** 438; Chem. Ztg. 1902, **26,** 391, Chem. Zts 1902, **1,** 89, 643; Mon. Sci. 1903, **59,** 5

[6] U. S. P. 1008725, 1911; abst. J. S. C. I 1912, **31,** 1470; C A 1912, **6,** 294; Mon Sci 1912, **77,** 159, Zts. Schiess. Spreng 1912, **7,** 81.

[7] G. King and M. Lindsley, U. S. P. 1012368, 1911; abst. J. S C. I. 1912, **31,** 92; C. A. 1912, **6,** 547; Chem. Ztg. Rep. 1912, **36,** 345; Mon. Sci. 1912, **77,** 159. The explosive of W. Snelling (U. S. P. 1343069, 1920; abst. C. A. 1920, **14,** 2420) is formed of ammonium nitrate 60, sodium nitrate 18, nitrostarch 12, rouge 8, and a hydrocarbon oil 2.

[8] E. P. 12743, 12744, 12745, 12746, 1912; abst. C. A. 1913, **7,** 3842; J. S. C. I. 1913, **32,** 991; Chem. Ztg. Rep. 1913, **37,** 614. See also E. P. 4940, 4941, 1913; abst. J. S. C. I. 1914, **33,** 712, 713.

or more anilids of the general formula RCO and NH_2, in which one of the hydrogen atoms of the amido group is replaced by an aromatic radical and in which the second hydrogen atom may be replaced by an aromatic or aliphatic radical. As an example the formula nitroglycerol 30%, nitrocellulose 65% and phenylacetamide 5% is given.

The apparatus for nitrating starch, as perfected by A. Ellis,[1] comprizes a nitrating tank, receptacles for nitrating acids and material to be nitrated, with connections therefrom to the nitrating tank and cooling coils around it, and a blower for forcing the finely divided starch through the supply connection into the closed nitrating tank, the latter having a hood to direct the particles downward into the acid.

J. Braunstein, as the result of his investigations upon the stabilization of nitrostarch, has obtained patent protection for the use as a nitrostarch stabilizer of sodium bicarbonate,[2] borax or an alkaline borate,[3] finely divided iron or iron filings,[4] either alone or in combination with lime,[5] or ammonium nitrate. Trojan Powder, a blasting powder used extensively in the building of the Panama Canal and composed of nitrostarch, ammonium nitrate, sodium nitrate and a stabilizer is the development of the patents of Braunstein referred to above.

Detonating explosives, in which nitrostarch is the essential ingredient have been patented by J. Braunstein and C. Waller and include the combination of nitrostarch with ammonium, sodium or barium nitrates and trinitrotoluene;[6] preferably with the addition of calcium carbonate[7] or paraffin oil.[8]

[1] U. S. P. 1003243, 1911; abst. J. S. C. I. 1911, **30,** 1232; C. A. 1911, **5,** 3911; Chem. Ztg. Rep. 1911, **35,** 595.

[2] U. S. P. 869051, 1907; abst. J. S. C. I. 1907, **26,** 1216; C. A. 1908, **2,** 913; Zts Schiess. Spreng. 1908, **3,** 116.

[3] U. S. P. 868636, 1907; abst. J S. C I. 1907, **26,** 1216; C. A. 1908, **2,** 912; Mon Sci 1909, **71,** 127; Zts. Schiess. Spreng. 1908, **3,** 55.

[4] U. S. P. 868637, 1907; abst. J. S. C. I. 1907, **26,** 1216; C. A. 1908, **2,** 912; Chem. Ztg. Rep 1907, **31,** 614; Zts. Schiess. Spreng. 1908, **3,** 55.

[5] U. S. P. 868638, 1907; abst. J. S. C. I. 1907, **26,** 1216; Chem. Ztg. Rep. 1907, **31,** 614; Zts. Schiess. Spreng. 1908, **3,** 55.

[6] U. S. P. 868837, 1907; U. S. P. 1188244, 1916; abst. C. A. 1916, **10,** 2150; J. S. C. I. 1916, **35,** 908; Mon. Sci. 1917, **84,** 56.

[7] U. S. P. 1188245, 1916; abst. C. A. 1916, **10,** 2150; J. S. C. I. 1916, **35,** 908; Mon. Sci. 1917, **84,** 56.

[8] U. S. P. 1188246, 1916; abst. C. A. 1916, **10,** 2150; J. S. C. I. 1916, **35,** 908. See also J. Braunstein, U. S. P. 868760, 1907; abst. C. A. 1908, **2,** 912; Mon. Sci. 1909, **71,** 127; Zts. Schiess. Spreng. 1908, **3,** 96.

Nitrostarch prepared according to the process of S. Sadtler[1] is formed by treating starch for two to four hours with a cold 1.5% solution of caustic soda in 2% of ordinary starch to remove the oil and proteins and swell the starch granules, rinsing with several changes of water, agitating with a 2% solution of bleaching powder (calculated on the weight of the starch) washing with water slightly acidulated with hydrochloric acid, drying and then nitrating the starch thus purified in a bath containing 65% of sulfuric acid, 25% nitric acid and 10% water, finally boiling the nitrated product first with water, then with a dilute sodium carbonate solution, finally following with prolonged washing with water to strict neutrality. The final product thus produced contains from 12 to 13 per cent. of nitrogen and is said to be more powerful as an explosive than nitroglycerol; is insensitive and cannot be exploded except by a detonator; does not yield injurious fumes upon combustion; is non-hygroscopic; insoluble in water, soluble in acetone and amyl acetate; denser than nitrocellulose and gelatinizes with nitroglycerol. However, where 5 to 6 per cent. of nitrocellulose is required for this purpose, 80 to 85 per cent. of nitrostarch may be used. One pound of dry starch produces 1.5 pounds of nitrostarch of a density of 1.57, giving an Abel heat test at 175° F. of 30 minutes and Sy stability test at 65° C. of one minute thirty-five seconds, and gave a potassium iodide starch test of 15 minutes at 70°.[2]

In the series of patents granted to Arthur Hough for the commercial manufacture of nitrated carbohydrates especially useful as explosives[3] he made a radical departure from the earlier methods in nitrating in the presence of but small amounts of water, taking advantage of the observation that when a carbohydrate has once been nitrated an increase of but little in nitration can be obtained only with the greatest difficulty, so that whatever degree of nitration is desired must be effected at the moment the carbohydrate comes in contact with the acids for the first time. In order to decrease the aqueous content of the nitrating bath free sulfuric acid was added at the beginning of nitration and provision was made for the further addition of anhydride to preserve the acidity during the entire step. He claims that by this proceeding a body is obtained containing as high as 16½% nitrogen which would indicate the product to be an octo-nitrate of starch. No investigator up to this time had been able to obtain nitrostarch containing so high a percentage of nitrogen. Hough dissolved the starch in nitric acid at a temperature of 90° F. and subsequently precipitated the nitrostarch by passing gaseous sulfuric anhydride, through the solution. In a latter patent[1] he altered the process by nitrating starch with a mixture of 3 parts of nitric acid of 95% monohydrate and 2 parts of 98% sulfuric acid, adding sufficient sulfuric anhydride to this so as to effect a concentration of 100% acidity with one to two per cent. of free sulfur trioxide in the solution. Further, during the process of nitration he injects more sulfuric acid having an excess of about 2% anhydride into the mixture and in this way obtains substantially a starch octonitrate.

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[1] U. S. P. 1211761, 1917; abst. J. S. C. I. 1917, **36**, 238; C. A. 1917, **11**, 1042; Mon. Sci. 1917, **84**, 60. Can. P. 170773, 1916; abst. C. A. 1918, **12**, 767.

[2] Met. Chem. Eng. 1917, **16**, 361; abst. C. A. 1917, **11**, 1750.

[3] U. S. P. 790840, 1905; abst. J. S. C. I. 1905, **24**, 691; Chem. Zts 1905, **4**, 331; Mon. Sci. 1905, **63**, 141; J. A. C. S. 1906, **28R**, 52.

C. Hoitsema[2] who had already studied the possibility of producing cellulose nitrates higher than the hexanitrocellulose by decreasing the water formed in the reaction by means of the addition of phosphoric anhydride, was unable to prepare products of as high nitration as 15%.

E. Berl and R. Bütler[3] have made experiments in the preparation of the highest nitrated starch according to the process described by Hough. They nitrated wheat, potato, rice and soluble starch according to the methods described by Hough, the finished products being examined with the following results:

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[1] U. S. P. 751076; abst. J. S. C. I. 1904, **23**, 385, Chem. Zts. 1904, **3**, 491; Mon. Sci. 1905, **63**, 15; J. A. C. S. 1904, **26R**, 401. E. P. 21171, 1902; abst. Arms and Explos. 1903, **11**, 17; J. S. C I. 1902, **21**, 1471; Chem. Zts. 1904, **28**, 111; Mon. Sci. 1905, **63**, 14. E. P. 12627, 1904; abst J. S. C. I. 1904, **23**, 950; Chem. Ztg. 1905, **29**, 1090; Mon. Sci. 1906, **65**, 135. F. P. 325196; abst. J. S. C. I. 1903, **22**, 650; Chem. Zts. 1903, **2**, 376; Mon. Sci. 1904, **61**, 16. F. P. 343907; abst. J. S. C. I. 1904, **23**, 113; Chem. Zts. 1904, **3**, 764; Mon. Sci. 1905, **63**, 86. D. R. P. 172549; abst. Mon Sci 1908, **68**, 47; Wag. Jahr. 1906, **52**, I, 471; Chem. Centr. 1906, **77**, II, 938; Zts. ang. Chem. 1906, **19**, 1055; Jahr. Chem. 1905–8, II, 851; Zts. Schiess. Spreng. 1906, **1**, 238. Norw. P. 14406.

[2] Zts. ang. Chem. 1898, **11**, 173; abst. J. S. C. I. 1898, **17**, 374; Wag. Jahr. 1898, **44**, 383; Chem. Centr. 1898, **69**, I, 780.

[3] Zts. Schiess. Spreng. 1910, **5**, 82; abst. C. A. 1910, **4**, 1556; J. S. C. I. 1910, **29**, 373; Chem. Zentr. 1910, **71**, I, 2074; Jahr. Chem. 1910, **63**, II, 412; Wag. Jahr. 1910, **56**, I, 495; Zts. ang. Chem. 1910, **23**, 1198. See also E. Berl and W. Smith, J. S. C. I. 1908, **27**, 534; abst. Chem. Zentr. 1908, **79**, II, 686; Jahr. Chem. 1905–8, II, 985.

Kind of Starch	% N	Flash Point	Solubility in		Hygroscopicity
			M. Alcohol	E. Alcohol	
Wheat	13.23	121	Insol	Difficultly	....
Potato...	13.44	120	Insol.	Difficultly	6.57%
Rice	12.86	135	Insol.	Soluble	......
Soluble...	13.35	120	Insol.	Soluble	......

The nitrostarches obtained by them are pure white products indistinguishable in appearance from the raw material, dissolving slowly in concentrated sulfuric acid, more readily by heat.[1] They were unable to confirm the statement of Hough as to higher nitration, and the stability of the nitrated starches prepared by them was low and not uniform. They found the nitrostarches to show great differences compared with the higher nitrated celluloses owing to their distinct hygroscopicity and this fact, of course, militates against their suitability in blasting technics. Their results led them to believe there exists a close relationship between the size of the molecules of the nitrates of cellulose and starch.

The nitrostarch made by the Nobel process, while it dissolves more easily in nitroglycerol, does not as completely gelatinize it as does pyroxylin, due to the low viscosity of the solution in acetone. Berl and Bütler nitrating potato starch by Hough's method obtained the following viscosities for solutions as compared with nitrocellulose nitrated in the same way, both containing 13.4% nitrogen:

	1% Solution	2% Solution	5% Solution
Potato starch nitrate	1.74	2.66	9.47
Cellulose nitrate	95.1	1,005	85,640

With other varieties of starch the viscosities were still lower. A distinct disadvantage of nitrostarch over nitrocotton is in the fact that it absorbs a much larger proportion of moisture from the atmosphere just as starch is more hygroscopic than cellulose. Thus Will found the following materials after being dried in an oven at 40° take up the amounts of moisture in an atmosphere nearly saturated at 25° as shown below:

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[1] This is contrary to the statement of the Hough patent specifications in which they are said to be but slightly soluble in sulfuric acid. According to Hough, best results are obtained when the starch is submitted to a purification process preliminary to nitration. This purification is best brought about by agitating the starch for several hours in a 1% sodium chloride solution containing 0.1% HCl at a temperature of 60°, which removes a hygroscopic material from the interior of the starch granule, to the extent of 5% on the weight of the starch. With this preliminary removal of the "hygroscopic" constituents, it then becomes possible to nitrate to a 16% nitrogen product, and also to greatly increase the stability.

	Hygroscopicity
Cotton	7 to 8%
Wheat starch	11.4%
Maize	10.6%
Potato	14.1%
Rice	11.4%
Soluble	11.3%

Corresponding figures for the nitrated products were found by Will and by Berl and Bütler to be:

	Per cent. N	Hygro-scopicity	Hygro-scopicity of Nitro-cotton with same Percentage N
Rice starch nitrate	8.51	7.37	6.1
Soluble starch nitrate	12 95	8.40	1 6
Potato starch nitrate	13 44	6 57	1 2

Nitrostarch has not been authorized for manufacture or importation into England. However, in the United States it is used in large amounts as a component of high explosives.

The defects in general of nitrostarch are the difficulty of inducing the proper stability, and the fact that nitrostarch can not be nitrated so highly.

A summary of the various methods propounded up to the present time for the preparation of acceptable nitrostarch are comprehended in the following generalizations:

1. A preliminary treatment of the starch by heating with dilute alkali to remove the oil, pectinous and mucilaginous matters.

2. Selection of a starch with the minimum of inorganic constituents (ash).

3. Removal of the maximum amount of water from the starch granule by previous drying at 105° to 115°, and preservation of this anhydrous state until the moment of immersion in the nitrating bath.

4. Solution of the starch in nitric acid of concentration and at a temperature so that a clear solution results. The concen-

tration of nitric acid and the temperature will depend upon the nature of the starch used and the amount of moisture contained therein. Upon the temperature, in a large measure, depends the amount of oxidation which the starch granule undergoes coincident with nitration.

5. The temperature of esterification must be kept sufficiently low so that nitration proceeds with the maximum uniformity for upon this, in a large measure, depends the question of ultimate stability. Microscopic examination of the nitrated starch granule shows that the exterior portion of the granule upon nitration gives a product which is much less deliquescent than is the nitration of the inner layers.

6. Precipitation of the nitrated starch in concentrated sulfuric acid should be conducted at a low temperature and with sufficient agitation of the acid so that the product is precipitated in a finely granular or flaky condition.

7. After the majority of the acid has been removed from the nitrated product, a preliminary acid boil, as in the stabilization of cellulose should be resorted to.

8. The defects which heretofore have been encountered in attempts to utilize nitrated starch in explosive combinations are the deliquescence of the nitrated starch and the instability, together with the fact of inferiority in percentage of nitrogen. However, in the manufacture of pyroxylin solutions for film formation, lacquers, bronzing liquids and the preparation of thermo-plastic combinations similar to celluloid and the pyroxylin plastics, nitrated starch of acceptable stability has distinct advantages over the corresponding nitrocellulose in that the fluidity of a given weight of nitrated starch in a simple or mixed solvent is much greater and hence the viscosity is less than that of a nitrocellulose, both esterified at the same temperature. Therefore in all those operations in which the solvent portion is not recovered, the starch nitrates, due to the fact that a larger amount of the same may be brought into solution with a decreased viscosity, offers advantages over the corresponding nitrated cottons or paper. The action of dilute nitric acid on starch has recently been exhaustively investigated.[1]

[1] O. De Conninck and Raynaud, Rev. gen. Chim. 1911, **14**, 169; abst. C. A. 1911, **5**, 2753; J. C. S. 1911, **100**, i, 607; Chem. Zentr. 1911, **82**, II, 272; Meyer Jahr. Chem. 1911, **21**, 194, 418. A. Doroschewski and A.

According to W. Snelling[1] *when nitrostarch (containing 12.8% N) 85 parts is mixed with cold "liquid" trinitrotoluene 15* parts only slight gelatinization is effected, the liquid TNT being merely spread over the surface of the nitrostarch granules. The mixture is then heated for about 15 minutes at a temperature of about 80°, and is thus converted into a tough colloidal mass which is said to be suitable as a smokeless powder, burning with great uniformity and being sufficiently tough to withstand the high pressure in guns without breaking up or producing erratic ballistic results.

C. Waller has described a granular uncompressed explosive suitable for use in blasting and having good water-resisting properties, comprized of nitrostarch 10%, sodium nitrate 73%, sulfur 7.5%, charcoal 7.5%, $CaCO_3$ and dried starch paste, each 1%.[2] Mononitronaphthalene may be added to the above to decrease the inflammability.[3] The W. Treese blasting explosive[4] is composed of nitrostarch 26%, yellow wax 13%, soap stock 7%, S 21%, niter 11%, and potassium chlorate 22%.

In the preparation of easily combustible paper, ordinary paper pulp is beaten with a substantial proportion of nitrostarch or nitrocellulose, and the material formed into paper in the usual manner. After sizing, it is preferred to add a quantity of insoluble calcium or magnesium salts (as the carbonates) which serves to increase the combustibility, or the paper may be impregnated with a nitrate (as $NaNO_3$) for the same purpose. Where extreme inflammability is aimed at, the paper may be formed of nitrocellulose entirely.[5]

N. Ceipek has described a nitrostarch made by the nitration

Rakowski, J. Russ. Phys. Chem. Soc. 1907, **39**, 427; abst. Chem. Zentr. 1907, **78**, II, 1325; C. A. 1907, **1**, 1542; J. C. S. 1907, **92**, i, 678; J. S. C. I. 1907, **26**, 1154; Jahr. Chem. 1905–8; II, 947. A. Doroschewski, A. Rakowski and A. Bardt, J. Russ. Phys. Chem. Soc. 1908, **40**, 932; abst. C. A. 1909, **3**, 1146; J. C. S. 1908, **94**, i, 767; Chem. Zentr. 1908, **79**, II, 1422; Jahr. Chem. 1905–8, II, 947.

[1] U. S P. 1305946, 1919; abst. C. A. 1919, **13**, 2130. U. S. P. 1310969, 1919; abst. C. A. 1919, **13**, 2450.

[2] U. S. P. 1305845, 1919; abst. C. A. 1919, **13**, 2130.

[3] C. Waller, U. S. P. 1305846, 1919; abst. C. A. 1919, **13**, 2130; J. S. C. I. 1919, **38**, 604-A.

[4] U. S. P. 1265975, 1918; abst. J. S. C. I. 1918, **37**, 488-A; C. A. 1919, **12**, 1700.

[5] C. Harrison and W. Bacon, E. P. 124516, 1916; abst. C. A. 1919, **13**, 1929. Nitrostarch is readily distinguished from unnitrated starch by moistening the sample with a drop of solution of iodine in potassium iodide

of powdered turmeric. The coloring matter having previously been extracted by boiling water, the starch is dried and nitrated in the usual manner.[1] To increase the explosive power and permanence of charging density and a decrease in hygroscopicity, a small amount of gelatinized nitrocellulose is recommended to be added.

In the United States, it is understood that the Ordnance Department has adopted starch nitrate in the form of "Trojan grenade explosive," "Trojan trench mortar shell explosive," and "grenite," not as a military or commercial explosive, the nearest approach to which is grenite, which is about 95% nitrostarch with the addition of binding material for facility in granulation. At the time the United States entered the recent war there was a marked shortage in TNT owing to insufficient toluene supply. As the culmination of a thorough investigation, it was determined that certain nitrostarch explosives, properly manufactured seemed to be entirely suitable for trench warfare purposes, but to offer advantages over TNT in a lower insensitiveness to rifle bullet fire, lower friction on impact, and ample supply of raw materials.

The two Trojan explosives, which are nearly the same in composition, contain approximately but 40% nitrostarch, the remainder being sodium and ammonium nitrates, and smaller amounts of materials added for the purpose of increasing stability, decreasing sensitiveness, or as antacids.

In the method of manufacture as carried out in the United States during the war, principally corn starch was nitrated, although it has been claimed that the nitration of cassava or tapioca starch results in the formation of a nitric ester of slightly higher stability. This point, however, is open to question, assuming the same purification treatment for each. The preliminary treatment of the starch for the elimination of impurities includes the solvent removal of fats and oil, exhaustive extraction with water in order to remove gums, pectin and similar materials, followed by careful and thorough drying at low temperatures,

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and examining under the microscope. The unnitrated granules are colored deep blue, whereas the nitrostarch granules remain colorless.

[1] E. P. 9743, 1911; abst. J. S. C. I. 1911, **30**, 926; Zts. Schiess. Spreng. 1912, **7**, 33. E. P. 13549, 1911; abst. C. A. 1912, **6**, 3525, J. S. C. I. 1911, **30**, 1232.

and disintegration by thorough screening after the mass has cooled.

In the nitrating process, the dried and cooled starch is slowly fed into the acid mixture in an iron nitrator provided with efficient agitation, and artificially cooled in order to regulate the temperature of esterification, and to guard against local preheating. The nitrated product is separated from the nitrating fluid in the usual manner, and washed and treated in general, except for certain mechanical changes due to the fine subdivision of the material, in a manner analogous to the nitration of cellulose, especially after pulping. The final drying usually takes place on trays in dry houses artificially heated, the temperature of the warm air seldom exceeding 35°–40°. The drying operation, and especially the handling and transportation of the warm, dry product is the most dangerous part of the process, the material in this condition being not only highly inflammable, but is capable of being ignited from a static charge, and, of course, when once ignited, it burns with explosive violence.

The incorporation of the dry nitrostarch with the doping or filling materials, as the inert portion of these explosives are usually termed, is a simple operation carried out in large revolving mixing barrels, each ingredient preferably being previously separately ground to the desired consistence or requisite fineness, and dried to the proper moisture content. Such granular explosives as grenite, are usually prepared by spraying a solution of the binding material upon the dry nitrostarch, while the latter is being agitated, the resulting granules being then dried and screened to desired size.

Nitrostarch—like the corresponding nitrated celluloses—preserves the appearance of the original material from which it is prepared, and cannot by visual inspection alone, be told from the unnitrated product. However, whereas starch is colored blue by iodine, nitrostarch is not; and whereas the former is gelatinized by means of hot water, the latter is unaffected; this is in addition to combustibility and solubility of the starch nitrates in ether-alcohol and in acetone. Nitrostarch, like the parent product is insoluble in cold water, less readily hydrolyzed by fungi, and ferments such as amylopsin. The nitrostarch usually produced ranges in nitrogen content of 12.5%–12.75%, that prescribed for military purposes containing a minimum of 12.8%.

The same difference is shown in starch and nitrostarch as is evident with cotton and nitrocotton, i. e., a reduced capacity for the absorption of atmospheric moisture, nitrated starch having a "normal hygroscopicity" of but 1%-2%, as against about 6%-10% for untreated starch.

It will be remembered that trench grenade and trench mortar shell explosives differ greatly in appearance and properties from straight starch nitrate, the former being of a gray to black color, of the consistency of brown sugar, showing a decided tendency to mat and compact upon compression due primarily to the small amount of mineral oil incorporated, which while decreasing the sensitiveness, at the same time partially counteracts the hydroscopicity of the deliquescent ammonium nitrate and other added ingredients. Notwithstanding this coating of water-repellent oil, Trojan explosives, when spread out in a thin layer in a damp atmosphere, attract moisture with such avidity as to become decidedly damp. Under the usual working conditions, however, little or no difficulty is experienced in loading explosives of this type, and in avoiding the absorption of an undue amount of moisture.

Grenite, which is almost entirely nitrostarch, differs markedly in appearance from the Trojan explosives, being in the form of small, white, hard granules which run freely without adhering. Since it contains no ammonium nitrate, the hygroscopicity is low, and there is little or no tendency to absorb moisture when placed in a damp atmosphere.

Pure, dry starch nitrate is more sensitive to impact than TNT, but less so than dry guncotton or nitroglycerol, and is readily detonated by a mercury fulminate detonator. Trojan explosives and grenite are both less sensitive than pure nitrated starch, being required to pass the pendulum friction test of the U. S. Bureau of Mines, and the rifle bullet test when packed in pasteboard containers. In heavy metal containers these explosives frequently ignite, burn when penetrated with a rifle bullet and occasionally explode.

Trojan explosives are said to be especially insensitive to ignition, being rather difficult to ignite with the flame of a match when spread out unconfined. Once ignited, however, it burns violently with a light-colored flame. In general, nitrostarch explosives are readily detonated by a number 6 mercury fulminate detonator containing one grain of mercury fulminate composition, this producing complete detonation unless the material has been rendered unduly insensitive by the absorption of an excessive amount of moisture, or from other causes.

An important consideration in the case of military explosives—primarily those intended for trench warfare—is their relative sensitiveness to explosion by influence, i. e., their susceptibility to detonation from the shock of a near by explosion. In this respect, it is claimed the Trojan explosives are especially insensitive.

Coming back once more to the question of nitrostarch stability, recent developments in the United States appear to have led to the production of a product which in this respect is highly satisfactory, and there is now every reason to believe that the nitrostarch explosives mentioned above as having been adopted by the Ordnance Department, possess excellent keeping properties when properly stored in a dry atmosphere at a reasonable temperature. If nitrostrarch powders of this general composition are allowed to absorb undue quantities of moisture, especially in a warm atmosphere, marked deterioration takes place owing to gradual decomposition and disintegration, but this does not result in a dangerous condition, for coincident with the deterioration is a corresponding diminution in explosive strength and sensitiveness.

When properly compressed, pure nitrostarch is said to detonate at probably a rate of not less than 20,000 feet per second. With the Trojan explosives, containing only about 25% nitrostarch, the rate of detonation is lowered, but the immense gas volume and great energy content makes this type of explosive quite suitable for trench warfare purposes. Trojan nitrostarch explosive has been used as a bursting charge for hand grenades, rifle grenades and the Stokes trench mortar shells. Although well adapted for the above purposes, it has not been recommended as a bursting charge for high explosive gun shells. Its physical consistence is such that it is necessary to load it into grenades by means of a vibrating machine, the explosive being "jarred" into the grenade through small funnel openings. Trench mortar shells are loaded by hand-stemming, or by means of a screw-filling machine.

Grenite has been approved only for grenades, and is considered too sensitive for use as a trench mortar shell explosive. Being granular and "free running," it is readily loaded into grenades through funnel openings, no attempt being made to pack it to a higher density. Nitrostarch explosives similar to the above have for many years been employed as blasting agents in mining, quarrying, and similar engineering operations, and have met with considerable success as efficient substitutes for the more expensive nitroglycerol explosives, for, unlike the latter, they are non-freezing.

The storage of nitrostarch is mainly a fire risk, i. e., the danger accompanying storage is more one of fire than explosion, although the fact must not be lost sight of that burning may become so energetic and fierce as to be almost explosive. Storage magazines are to be kept at as low a temperature as possible, and in a reasonably dry atmosphere, on account of the deliquescent nature of the ammonium nitrate contained therein. The handling of this class of explosives is practically devoid of danger.

The chemical composition of Trojan explosives and grenite, as prescribed by the U. S. Ordnance Department, is said to be:

	Trojan Explosive	Grenite
Nitrostarch	23%-27%	95.5%-98 25%
Ammonium nitrate	31%-35%	
Sodium nitrate	36%-40%	
Charcoal	1 5%-2 5%	
Heavy hydrocarbons	0 5%-1 5%	0 75%- 2 00%
Antacid	0 5%-1 5%	
Diphenylamine	0 2%-0 4%	
Gum arabic		0 75%-2%
Moisture	0.-1 2%	0-1 0%

The Ordnance Department specifications prescribe the following methods for the analysis of Trojan explosive, which are equally applicable to other explosives of this general nature:

(a) *Moisture.* A 5 gm. sample is spread evenly on a 90 mm. (3.5") watch glass, placed in a desiccator over conc. H_2SO_4 for 48 hours, loss in weight being taken as moisture. Or a vacuum desiccator may be used with H_2SO_4, sp. gr. 1.84, employing a vacuum of at least 700 mm. mercury for 48 hours, the vacuum being slowly relieved and the loss in weight being taken as moisture. Limit of moisture, 1.2%.

(b) *Ether Extract.* A 10 gm. sample is placed in a Gooch crucible with thin asbestos mat, and extracted with pure petroleum ether (sp. gr. 0.64-0.66) to completion. The crucible is dried by means of a stream of dry air, then dried in a steam oven at about 70°. Loss in weight, after deducting the moisture, is taken as heavy hydrocarbon oil present, together with diphenylamine. The latter may be estimated by means of the Dumas method of nitrogen determination.

(c) *Water Extract.* The material in the crucible after removal of the hydrocarbon oil consists of nitrostarch, sodium and ammonium nitrates, charcoal and $NaHCO_3$. Treatment with warm distilled water removes all the inorganic salts, which can be determined in the aqueous extract by the usual quantitative methods. After drying at 80° until constant weight, the residue in the crucible consists of nitrostarch and charcoal.

(d) *Sodium Bicarbonate.* The aqueous extract is made up to a definite volume, and an aliquot portion taken and titrated with $N/10$ H_2SO_4 using methyl orange as indicator.

(e) *Ammonium Nitrate.* An aliquot portion of the water extract is taken, caustic soda added to strong alkalinity, and distilling in the usual manner, titrating the distillate with standard acid and methyl orange as indicator.

(f) *Sodium Nitrate.* An aliquot portion of the aqueous extract is acidified with HNO_3, and the solution evaporated to dryness in a platinum dish. It is then ignited at a low red heat over a suitable flame, using care to avoid loss of contents by spirting. The weight is then taken and a correction made for the amount of sodium bicarbonate present, and the results regarded as sodium nitrate present. Following this procedure the ammonium nitrate would be taken by difference, in order to obviate the determination of ammonia.

(g) *Charcoal.* The residue in the Gooch crucible after the water extraction consists of nitrostarch and charcoal. The material is best extracted in a Wiley extractor with warm acetone until no further soluble material is obtained. Dry the crucible and contents at not to exceed 100°. The weight of the charcoal is taken as the increase in the weight of the crucible over its original empty weight.

(h) *Nitrostarch.* The difference between the sum of nitrostarch and charcoal content as determined in (c), and the percentage of charcoal as found by (g), represents the nitrostarch present.

The analysis of grenite is carried out in a similar manner, the ether extraction removing the oil, the water extraction dissolving the gum arabic, and leaving nitrostarch as the residue.

Nitrates of the Carbohydrates. After Braconnot had announced his discovery of the formation of a combustible and explosive body from the action of nitric acid upon starch, carbohydrates, and especially the sugars were extensively investigated by the earlier chemists because these nitrated products could conveniently be crystallized or otherwise purified and their composition arrived at with more definiteness than with the corresponding analogous colloidal celluloses or starches.

L. Svanberg and Staaf[1] have nitrated licorice sugar and superficially examined the chemical composition of the nitroglycyrrhizin thus produced. H. Hlasiwetz and L. Pfaundler[2] in 1864 published their results upon the nitration of dulcite and isodulcite, the latter being described as a hard, white mass, insoluble in water, readily soluble in alcohol, difficultly crystallizable, melting below 100° and detonating weakly on percussion. L. Svanberg and Staaf[3] and G. Gé[4] described bodies obtained by the nitration of lactose. Gé obtained a lactose-pentanitrate in the form of transparent plates when deposited from alcohol, which melted at 139.2°, decomposed at 90° and exploded at 155.5°; sp. gr. at zero, 1.684; soluble in 6.9 parts boiling and 63.3 parts cold ethyl alcohol; insoluble in water. A lactose trinitrate was also obtained as a gummy mass melting at 36.8°, detonating at 110°, sp. gr. at zero 1.479.[5]

H. Vohl in his work on inosite[6] and on nitroinosite,[7] dis-

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[1] Oefvers. af K. Acad. Vet. Forhandl. **5**, 4, abst. Berz. Jahr. Chem. 1849, **28**, 361.

[2] Ann. 1863, **127**, 362; abst. Chem Centr. 1864, **35**, 55, 463; Wien Akad Ber. **48**, II, 19; Bull. Soc. Chim. 1864, **1**, 204; Jahr. Chem. 1863, **16**, 585; J. prakt. Chem. 1863, **90**, 452, Zts. Chem 1863, **6**, 604.

[3] Oefvers. af K. Acad. Vet. Förhandl. **4**, 171, abst. Berz Jahr Chem. 1849, **28**, 360.

[4] Jour. Russ. Phys. Chem. Soc. 1882, **14**, 253; abst. Jahr. Chem. 1882, **35**, 1121; Ber. 1882, **15**, 2238; Chem. Centr. 1882, **53**, 707; Bull. Soc. Chim. 1882, **38**, 138.

[5] See also the nitrolactose or nitrolactine of M. Sjöberg. F. P. 192683, 1888; abst. Mon. Sci. 1889, **33**, 633. The explosive of H. Kölf (E. P. 8811, 1890; abst. J. S. C. I. 1891, **10**, 573) comprized a smokeless gunpowder made from a carbohydrate incorporated with a dinitrocompound.

[6] Ann. 1856, **99**, 125; abst. J. prakt. Chem. 1856, **69**, 299; Ann. Chim.

solved inosite in concentrated nitric acid as long as any passed in solution, the nitrocompound being then precipitated by means of concentrated sulfuric acid; crystallizes from alcohol in anhydrous rhombohedras, is insoluble in water but readily soluble in ether, chloroform, ethyl acetate, amyl acetate and acetylene tetrachloride. When recrystallized from alcohol a crystalline mass was obtained, depositing without water of crystallization, which sublimes without residue and detonates by percussion.

In endeavoring to determine the probable instability of cellulose nitrate, the following summary, as condensed by C. Cross and E. Bevan,[1] represents the more important results:[2]

Monoses. The *aldoses* are fully esterified, in the pentoses 4OH, in the hexoses 5OH groups reacting. The pentose nitrates are comparatively stable at 50°; the hexose nitrates on the other hand are extremely unstable, showing a loss of weight of 30%–40% when kept twenty-hour hours at this temperature.

"Xylose is differentiated by tending to pass into an anhydride form $(C_6H_{10}O_5)n - H_2O$ under this esterification. When treated in fact with the mixed acids, instead of by the process usually adopted by the authors of solution in nitric acid and subsequent addition of the sulfuric acid, it is converted into the dinitrate $C_5H_6O_2.(NO_3)_2$.

"*Ketoses* (C_6). These are sharply differentiated from the corresponding aldoses by giving *tri*nitrates $C_6H_7O_2(NO_3)_3$ instead of *penta*nitrates, the remaining OH groups probably undergoing

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Phys. 1856, **48**, 380; Arch. ph. nat. **33**, 153; Jahr. Chem. 1856, **9**, 669. Ber. 1874, **7**, 106; Amer. Chemist, 1874, **4**, 165, 470; J. C. S. 1874, **27**, 463; Jahr. rein Chem. 1874, **2**, 175; Rev. Sci. 1874, **3**, 1216. In the process for the manufacture of envelopes for storage batteries as disclosed by E. Sperry (U. S. P. 723329, 1903; abst. J. S. C. I. 1903, **22**, 560; J. A. C. S. 1903, **25R**, 494) vegetable fiber is prepared to form a fabric for envelopes for storage batteries by first removing the oily and starchy matter from the fiber, drying and nitrating in such a manner as to nitrate the carbohydrates, using for this purpose a mixture of 113.5 parts nitric acid (sp. gr. 1.42) and 150 parts sulfuric acid (sp. gr. 1.84) at a maximum temperature of 78° F. After nitration the fabric is washed and treated with nitrobenzene.

[7] Ann. 1858, **105**, 330; abst. J. prakt. Chem. 1858, **75**, 125; Chem. Centr. 1858, **29**, 446; Jahr. Chem. 1858, **11**, 489.

For nitrated dambonite, see P. Champion, Compt. rend. 1871, **73**, 114; J. C. S. 1871, **24**, 811; Zts. Chem. 1871, **14**, 348; Bull. Soc. Chim. 1871, **16**, 301; Jahr. Chem. 1871, **24**, 800.

[1] "Researches on Cellulose," 1895–1900, p. 42.

[2] See also C. Cross, E. Bevan and Jenks, Ber. 1901, **34**, 2496; abst. Chem. News, 1901, **84**, 61; J. C. S. 1901, **80**, i, 672; J. S. C. I. 1901, **20**, 1133; Bull. Soc. Chim. 1902, **28**, 130; Chem. Centr. 1901, **72**, II, 882; Jahr. Chem. 1901, **54**, 892.

internal condensation. The products are, moreover, *extremely stable.* It is also noteworthy that levulose gave this same product, the trinitrate of the anhydride (levulosan) by both methods of nitration.

"The *Bisaccharides* or *Bioses* all give the octonitrates. The degree of instability is variable. Cane-sugar gives a very unstable nitrate. The lactose nitrate is more stable. Thus at 50° it loses only 0.7% in weight in eight days; at 75° it loses 1% in twenty-four hours, but with a rapid increase to 23% in fifty-four hours. The maltose octonitrate melts (with decomposition) at a relatively high temperature, 163°-164°. At 50°-75° it behaves much like the lactose nitrate.

"*Trisaccharide.* Raffinose yielded the product $C_{18}H_{21}O_5.(NO_3)_{11}$.

"*Starch* yields the hexanitrate (C_{12}) by both methods of nitration. The product has a high melting and decomposing point, viz., 184°, and when thoroughly purified is quite stable. It is noted that a yield of 157% of this nitrate was obtained, and under identical conditions cellulose yielded 170%.

"*Wood gum,* from beech wood, gave a tetranitrate (C_{10} formula) insoluble in all the usual solvents for this group of esters.

"The authors point out in conclusion that the conditions of instability and decomposition of the nitrates of the monosetriose series are exactly those noted with the cellulose nitrates as directly prepared and freed from residues of the nitrating acids. They also lay stress upon the superior stability of the nitrates of the anhydrides, especially of the ketoses."

W. Will and F. Lenze[1] have investigated the nitric esters of bioses, trioses, pentoses and hexoses, all well-characterized carbohydrates, as well as the mono-saccharides (monoses) di-saccharides (bioses), tri-saccharides (trioses) and poly-saccharides, the methods of nitration employed being designed to introduce the maximum amount of nitrogen. Starch, wood gum and other celluloses were also experimented with in order to obtain comparable results. In order to throw light on the nature of the by-products resulting from the nitration of cellulose, they investigated specifically the behavior of various carbohydrates towards a mixture of concentrated nitric and sulfuric acid, it having been observed that cellulose is resolved into sugar under the hydrolyzing action of dilute acids. The nitrates obtained by this means are readily oxidized by Fehling's solution and rotate the plane of polarized light. They dissolved in acetone, acetic acid and ethyl alcohol but are practically insoluble in water and in petroleum, as well as in cold concentrated hydrochloric acid, undergoing decomposition in this latter liquid when heated, chlorine being liberated. Boiling water gradually decomposes them, eliminating oxides of nitrogen with slow degradation of the product. The following bodies were specifically investigated:

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[1] Ber. 1898, **31**, 68; abst. J. C. S. 1898, **74**, i, 227; Chem. News, 1898, **77**, 152; J. S. C. I. 1898, **17**, 271; Bull. Soc. Chim. 1890, **20**, 390; Chem. Centr. 1898, **69**, I, 441; Jahr. Chem. 1898, **51**, 1307; Wag. Jahr. 1898, **44**, 707; Zts. ang. Chem. 1898, **11**, 517.

Rhamnose tetranitrate, $C_6H_8O_5(NO_2)_4$, separates from alcohol in colorless, rhombic crystals and melts at 135°, decomposing at 136°; a 2.3 per cent.[1] solution in methyl alcohol has $[\alpha]_D = -68.4°$. The trinitrate is amorphous, m. pt. around 100°. Insoluble in water, soluble in alcohol and ether.

Arabinose tetranitrate, $C_5H_6O_5(NO_2)_4$, is deposited by alcohol in monoclinic crystals and melts at 85°, decomposing at 120°; a freshly prepared 4.4 per cent. solution in alcohol has $[\alpha]_D = -101.3°$ which drops to $-90°$ after 20 hours. Insoluble in water; easily soluble in methyl or ethyl alcohol, acetic acid or acetone.

Xylose anhydride dinitrate, $C_5H_6O_4(NO_2)_2$, crystallizes from alcohol in spherical aggregates and melts at 75°-80°. *l*-Xylose tetranitrate, crystals, m. pt. 141°.

Glucose pentanitrate, $C_6H_7O_6(NO_2)_5$, is an amorphous powder which melts at 10°, decomposing at 135°; it dissolves very readily in alcohol and is insoluble in water and petroleum. In a 6 per cent. alcoholic solution, it has $[\alpha]_D = 98.7°$; it reduces Fehling's solution when heated with it.

Galactose pentanitrate, $C_6H_7O_6(NO_2)_5$, occurs in two forms.

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[1] A rhamnose (isodulcit, rhamnodulcit, hesperidin sugar) trinitrate, amorphous, has been described by H. Hlasiwetz and L. Pfaundler, Ann. 1863, **127**, 364; abst Chem. Centr. 1864, **35**, 55, 463; Wien. Akad. Ber. **48**, II, 19; Bull. Soc. Chim. 1864, **1**, 204; Jahr. Chem. 1863, **16**, 585; J. prakt. Chem. 1863, **90**, 452; Zts. Chem. 1863, **6**, 604. W. Stone (Amer. Chem. J. 1896, **15**, 653) and G. Chavanne (Compt. rend. 1902, **134**, 661) have described arabinose tetracetate.

Nitromannite has been investigated by Tischanowitz (Jahr. Chem. 1864, **17**, 583); Sokoloff (Bull. Soc. Chim. 1882, (2), **38**, 138); Strecker (Ann. 1850, **73**, 59); Ann. Chim. Phys. 1875, (5), **6**, 125); Kachler (Ber. 1886, **19R**, 748); Busolt (Jahr. f. Landw. 1913, 159); and M. Berthelot (Bull. Soc. Chim. 1885, (2), **43**, 538).

The α-modification dissolves less readily in alcohol, from which it crystallizes in slender, transparent needles, and melts at 115°-116°, decomposing at 126°; a 4 per cent. solution in alcohol has $[\alpha]_D$ = 124.7°. The β-compound crystallizes in monoclinic needles, melts at 72°-73°, and decomposes at 125°; a 6.7 per cent. solution in alcohol has $[\alpha]_D$ = —57°.

Mannose pentanitrate crystallizes from absolute alcohol in transparent, rhombic needes, melts at 81°-82°, and decomposes at 124°; a 5 per cent. solution has $[\alpha]_D$ = 93.3°.

Levulosan trinitrate, $C_6H_7O_5(NO_2)_3$, is produced in two distinct forms. The α-modification crystallizes from alcohol in lustrous needles, melts at 137°-139°, and decomposes at 145°; a 1 per cent. solution in methyl alcohol has $[\alpha]_D$ = +62°. The β-compound crystallizes in spherical aggregates, melts at 48°-52°, and decomposes at 135°; a 5 per cent. solution in alcohol has $[\alpha]_D$ = 20°.

Sorbinosan trinitrate, $C_6H_7O_5(NO_2)_3$, melts indefinitely at 40°-45°.

a-Glucoheptose hexanitrate, $C_7H_8O_7(NO_2)_6$, crystallizes from alcohol in transparent needles and melts at 100°; a 3.4 per cent. solution in alcohol has $[\alpha]_D$ = +104.8°.

a-Methylglucoside tetranitrate, $C_7H_{10}O_6(NO_2)_4$, crystallizes from alcohol in lustrous, quadratic plates, melts at 49°-50°, and decomposes at 135°; a 6.2 per cent. solution in alcohol has $[\alpha]_D$ = 140°.

Methyl-*d*-mannoside tetranitrate crystallizes from alcohol in slender needles resembling asbestos and melts at 36°; a 2.5 per cent. solution in alcohol has $[\alpha]_D$ = 77°.

Saccharose octonitrate, $C_{12}H_{14}O_{11}(NO_2)_8$, crystallizes in spherical aggregates, melts at 28°-29° and decomposes at 135°; a 3.4 per cent. solution in alcohol has $[\alpha]_D$ = 52.2°.

Lactose octonitrate, $C_{12}H_{14}O_{11}(NO_2)_8$, crystallizes from alcohol in leaflets and melts at 145°-146°; a 2.8 per cent. solution in methyl alcohol has $[\alpha]_D$ = 74.2°. This compound closely resembles the pentanitrate described by Gélis.[1] The hexanitrate melts at 81°.

Maltose octonitrate, $C_{12}H_{14}O_{11}(NO_2)_8$, crystallizes from alcohol in lustrous needles and melts and decomposes at 163°–164°; a 3.5 per cent. solution in glacial acetic acid has $[\alpha]_D = 128.6°$.

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[1] J. Russ. Phys. Chem. Soc. 1882, **14**, I, 253; abst. Ber. 1882, **15**, 2238-R.

Trehalose octonitrate crystallizes from alcohol in nacreous leaflets, melts at 124°, and decomposes at 136°; a 4 per cent. solution in glacial acetic acid has $[\alpha]_D = 173.8°$.

Raffinose undecanitrate, $C_{18}H_{21}O_{16}(NO_2)_{11}$, separates from alcohol in amorphous, spherical aggregates, melts indefinitely at 55°–65°, and decomposes at 136°; a 3.6 per cent. solution in alcohol has $[\alpha]_D = +94.9°$.

b-Glucosan trinitrate, $C_6H_7O_3(NO_2)_3$, crystallizes from alcohol in lustrous needles and melts at 101°; a 2.4 per cent. solution in alcohol has $[\alpha]_D = 61.4°$.

A hexanitro-derivative of starch, $C_{12}H_{14}O_{10}(NO_2)_6$, is an amorphous powder which decomposes at 194° without previously melting.[1]

Wood gum also yields a nitro-derivative.[2]

R. Kändler[3] has proposed as an explosive a combination of sodium or potassium nitrate with a nitro-carbohydrate and a nitro-hydrocarbon, the former being incorporated in the mixture in the form of an alcoholic solution and the nitro-hydrocarbon dissolved in water.

The explosive composition as proposed by H. Hibbert[4] embraces the solution of a carbohydrate in a mixture of 1.2-glycols, containing, ethylene, propylene, and butylene glycols and polyglycols, nitrating the resulting solution to produce a mixture of nitro-carbohydrate, nitrated 1.2-glycols and nitrated polyglycols.

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[1] O. Mühlhauser, Dingl. Poly. 1892, **284,** 137; abst. J. C. S. 1893, **64,** i, 6; Jahr. Chem. 1892, **45,** 2732; Wag. Jahr. 1892, **38,** 374; Chem Tech. Rep. 1892, **31,** I, 223; Meyer Jahr. Chem. 1892, **2,** 364; Tech. Chem. Jahr 1892–1893, **15,** 174. For *d*-fructose pentanitrate, see W Will and F. Lenze, Ber. 1898, **31,** 68. E. Berl and W. Smith, J. S. C. I. 1908, **27,** 534; Chem. Zentr. 1908, **79,** II, 686; the *d*-fructose trinitrate melts at 135°–139°.

[2] R. Bader, Chem. Ztg. 1895, **19,** 55, 78; abst. J. C S. 1896, **70,** i, 335; Ber. 1895, **28,** 427-R; Chem. Centr. 1895, **66,** I, 373; Jahr. Chem. 1895, **48,** 1297.

[3] E. P. 20799, 1900; abst. J. S. C. I. 1901, **19,** 1240 Other nitrates which have been more or less imperfectly described, are: quercin (quercinit, cocosit, scyllit) nitrate, rhombohedric crystals. *d*-Inosit-methyl ether (pinit, matezit, sennit, cathartomannite) pentanitrate, amorphous. Dimethylinosite (dambonit), nitrate explosive (A. Girard, Compt. rend. 1871, **73,** 426; Zts. Chem. 1871, 335). *i*-Inosit (phaseomannit, nucit), hexanitrate, (H. Vohl, Ber. 1874, **7,** 106). *d*-Quercit (cyclite) pentanitrate (V. Dessaigne, Compt. rend. 1851, **33,** 462. F. Homann, Ann. 1878, **190,** 282), amorphous. Volemit gives an oily nitrate (E. Bourquelot, J. Pharm. (6), **2,** 385; Zts. d. Ver. 1895, II, 953). Mannoheptit heptanitrate, needles, m. pt. 138°. Styracit tetranitrate, explosive. Dulcit (melampyrit, dulcin, dulcose) nitrate. (C. Vincent and Delachanal, Compt. rend. 1889, **108,** 354); dulcit hexanitrate (A. Bechamp, Compt. rend. 1860, **51,** 257), needles, m. pt. 68–72°. Arabite (pentite, lyxit) pentanitrate, syrup (L. Vignon and F. Gerin, Bull. Soc. Chim. 1902, **27,** 30). Levulin (laevosin, secalin, secalose) nitrate, colorless crystals. Trehelose (mycose) octonitrate, leaves, m. pt. 124°.

[4] U. S. P. 1231351, 1917; abst. J. S. C. I. 1917, **36,** 943; C. A. 1917,

In endeavors to nitrate the natural occurring gums into products of commercial utility P. Champion[1] nitrated the Dambonit, which is a saccharine substance, isolated by A. Girard from Gambon rubber,[2] and found the nitroproduct obtained readily crystallizable from hot alcohol, insoluble in water and detonating on precussion. Dambose shows the same behavior and also gives a nitro-compound, crystallizing from alcohol which explodes with still greater force than the dambon nitrate and like nitrodulcite decomposes below 100°, evolving yellow vapors.

W. Will and F. Lenze[3] prepared wood gum nitrate with 12.91 per cent. N, obtaining it in the form of an almost colorless, corneous mass, which was found to be insoluble in acetone and acetic ester.

Nitrosaccharose (Nitrosugar, Nitrofulmin, Fulminating sugar, Glucodine). L. Svanberg,[4] H. Reinsch,[5] H. Vohl,[6] A. Sobrero,[7]

11, 2407; Mon Sci. 1918, **85,** 83. In the process of G. Anchors (U. S. P. 1329353, 1920, abst J S. C. I. 1920, **39,** 249-A) carbohydrates are puffed, then nitrated, and the products are treated with salts of fatty acids.

[1] Compt rend 1871, **73,** 114; abst Zts. Chem. 1871, **14,** 348; Bull. Soc Chim. 1871, **16,** 301; Jahr. Chem. 1871, **24,** 800; Amer. Chemist, 1871, **2,** 311.

[2] Compt rend. 1868, **67,** 820; abst. Jahr. Chem. 1868, **21,** 771; Zts. Chem 1868, **11,** 66, J. prakt. Chem. 1869, **107,** 266; Bull. Soc. Chim. 1869, **11,** 498.

[3] Ber 1898, **31,** 89; J. C. S. 1898, **74,** i, 227; Chem. News, 1898, **77,** 152.

[4] Öfvers. K Vet. Acad. Forhandl. 1847, **4,** 51, 214; abst. Berz. Jahr. Chem 1848, **27,** 389; Chem. Centr. 1848, **19,** 702. Skand. Naturf. Förhandl. 1848, **5,** 337. See also L Thompson, Pharm. Trans. **8,** 166; J. pharm. 1848, **13,** 103; J. Chem. Med. (3), **5,** 69, 180; Jahr. Chem. 1847–8, **1,** 1146. C. Schoenbein, Pogg. Ann. 1847, **70,** 100. H. Reinsch, J. prakt. Chem. 1849, **47,** 477. H. Vohl, Ann. 1849, **70,** 360. A. and W. Knop, J. prakt. Chem. 1852, **56,** 334.

[5] Jahr. f. pract. Pharm. **18,** 102; abst. Berz. Jahr. Chem. 1851, **30,** 370. C. Dittmar (U. S. P. 252600, 1882) has described an explosive compound consisting in the formation of chlornitrosaccharose by dissolving cane sugar or sucrose in chlorhydrin, and then converging into a nitro compound by nitric and sulfuric acids. The product requires a strong exploding-cap or detonation. When combined with nitrocellulose, no exploding-cap is said to be required.

[6] Ann. 1849, **70,** 360; abst. Jahr. Chem. 1849, 470; Ann. 1858, **105,** 330; abst. J. prakt. Chem. 1858, **75,** 125; Chem. Centr. 1858, **29,** 446; Jahr. Chem. 1858, **11,** 489. See also G. Gelis (J. Russ. Phys. Chem. Soc. 1882,

A. and W. Knop[1] and C. Schönbein,[2] are among the earlier investigators who have studied this substance and suggested technical uses for it, but such suggestions have, as yet, met but very little success.

In 1892 a careful investigation of nitrosaccharose was made by A. Elliot[3] who prepared this body by acting upon 95 gms. of sugar with 800 gms. of sulfuric acid, sp. gr. 1.84 and 300 gms. of nitric acid, sp. gr. 1.53, the whole being cooled after the sugar has been added to the acid mixture. After the balance of the sugar has been incorporated, the completed mixture is allowed to stand an hour with frequent stirring, after which the acids are poured off from the nitrosaccharose and the latter washed and thoroughly kneaded with water, weight 135 gms. Upon standing with water the nitrosaccharose becomes slightly acid and gave an odor smelling faintly of hydrocyanic acid. Elliot made the following observations on the reaction of solvents on the nitrosaccharose prepared by him: Insoluble in cold, and soluble in hot water; soluble in both cold and hot absolute alcohol and in alcohol of 93%; slightly dissolved in 80% cold alcohol; readily so in hot 80% or 50% alcohol; soluble in both cold and hot ether, chloroform, sulfuric acid of 1.84 sp. gr., acetic acid, wood naphtha, nitrobenzene, concentrated nitric acid, ethyl acetate and acetone; insoluble in cold and soluble in hot benzene, amyl alcohol, phenol, toluol, olive oil, sperm oil, glycerol and hydrochloric acid; insoluble in cold and hot carbon bisulphide, turpentine, petroleum, naphtha of 71°-76° Bé., Astral oil and mineral oils; readily decomposed by stannous chloride, ferrous sulfate, ferric chloride and

14, I, 253; abst. Ber. 1882, **15,** 2238), who obtained two lactose nitrates, one supposedly a penta- and the other a trinitrate. Lambotte (F. P. 152285, 1882; abst. Mon. Sci. 1883, **25,** 617) nitrates cane sugar, then combines with carbon bisulfide, lead oxide, sawdust and barium sulfate, in the preparation of an explosive.

7. Compt. rend. 1847, **24,** 247; abst. Berz. Jahr. 1849, **28,** 358; Jahr. Chem. 1847-8, **1,** 1145.

[1] J. prakt. Chem. 1852, **56,** 334; abst. Jahr. Chem. 1852, **5,** 657; Chem. Centr. 1852, **23,** 129, 423. In E. P. 20467, 1893 (abst. J. S. C. I. 1893, **12,** 973; 1894, **13,** 1010), A. Nobel has described the properties of an explosive composed of nitrocellulose dissolved or incorporated with a mixture of nitrosugar, nitroglycerol, mononitronaphthalene, dinitrobenzene, di- or trinitrotoluene, potassium chromate, and potassium ferrocyanide, designed as a blasting or mining fuse.

[2] Pogg. Ann. 1847, **70,** 100; abst. Berz. Jahr. 1849, **28,** 358; Jahr. Chem. 1847-8, **1,** 1146.

[3] J. A. C. S. 1882, **4,** 147; abst. Proc. U. S. Naval Inst. 1882, **8,** 449; Chem. Tech. Mitth. 1882-3, **32,** 96.

ammonium sulfide. He found that ferrous chloride in the presence of hydrochloric acid reduces nitrosaccharose and converts the sugar into glucose; that ammonium sulfhydrate reduces nitrosaccharose without converting the sugar, or only to a very slight extent. A. Elliot[1] gives the true formula for nitrosaccharose as $C_{12}H_{14}(O.NO_2)_8O_3$ or an octonitrate, thus coming into the same class of organic nitrates as nitrocellulose and nitroglycerol.

The year previously, J. Bonneville[2] obtained provisional protection only for a process in which vegetable fiber is first steeped in a hot solution of sugar and after drying is nitrated in the usual manner, this co-nitration of fiber and sugar being intended primarily for use as varnish when dissolved in hot acetic acid or methylated spirit.

The "Explosive Resin" patented by Pellier[3] was composed of nitrated cane or beet sugar combined with lime and then treated with dilute or concentrated hydrochloric acid, the resultant product being described as a yellowish explosive powder.

Lewin[4] has patented an explosive combination to which the name Sandholite was bestowed and composed of nitroglycerol, nitrocellulose, nitrosaccharose, rye meal, sodium nitrate and paraffin.

The "Kolf Smokeless Powder,"[5] under which application was made in England for license under the name Kolf's Blasting Powder, is said to have the following composition: Nitrocarbon (perhaps nitrohydrocarbon) 50%; nitrosugar 38%; nitroglycerol 8%; saltpeter 2%; aniline (as a stabilizer) 2%.

In 1898, W. Will and F. Lenze,[6] re-investigated nitrosaccharose and obtained a colorless resin-like mass of low stability and melting at 30°, decomposing at 135° and containing 15.79% nitrogen. The theory called for 15.95% nitrogen for an octonitrate.

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[1] J A. C. S. 1882, **4,** 186; abst Proc. U. S. Naval Inst. **8,** 449; Chem. Tech Mitth. 1882-3, **32,** 96.

[2] E P. 814, 1881; abst. Chem. Ind. 1881, **4,** 139.

[3] F. P. 180555, 1886; abst. Mon. Sci. 1888, **31,** 113. The explosive "Petragit" proposed by Doutrelepont and Schreiber consists of nitrosaccharose, 38.6%; nitrolignin, 5%; and potassium nitrate, 56.4%.

[4] F. P. 185956, 1887, abst. Mon. Sci. 1888, **32,** 883. His product was called "Sandholite." Compare A. Cocking and Kynoch, Ltd., E. P. 2836, 17221, 1911; abst. C. A. 1912, **6,** 1992; 1913, **7,** 417; J. S. C. I. 1912, **31,** 303, 954; Chem. Ztg. Rep. 1912, **36,** 382; Zts. Schiess. Spreng. 1912, **7,** 269, 332, who co-nitrate sugar and glycerol.

[5] H. Kolf, E. P. 8811, 1890; abst. J. S. C. I. 1891, **10,** 573; 22739, 1892; abst. J. S. C. I. 1893, **12,** 1057. Cf. Nitrosaccharine, Phot. Corr. 1866, **3,** 185. D. R. P. 62159; abst. Wag. Jahr. 1892, **38,** 377; Zts. ang. Chem. 1892, **5,** 435; Ber. 1892, **25,** 711-R; Mon. Sci. 1892, **39,** 288. D. R. P. 56786; abst. Zts. ang. Chem. 1891, **4,** 306; Jahr. Chem. 1891, **44,** 2667; Wag. Jahr. 1891, **37,** 434; Ber. 1891, **24,** 1005-R.

[6] Ber. 1898, **31,** 81; abst. J. C. S. 1898, **74,** i, 227; Jahr. Chem. 1898, **51,** 1307.

The explosive "Glukodine" is a whitish liquid produced by the nitration of a saturated solution of cane sugar in glycerol. Free sugar dissolves in it and in turn it is entirely soluble in ether. Two varieties of Glukodine powder are made, white and black. Samples of both analyzed are said to have shown the following composition:

	White	Black
Matter soluble in ether (Glukodine).....	36.4%	34.24%
Free Sugar...	8.4%	8.76%
Sodium Salts (mostly sodium nitrate) ...	31.2%	37.84%
Nitrocellulose.....	23.36%	......
Nitrocellulose and charcoal	....	19.31%

Another analysis of the same sample showed that the Glukodine in the white powder consisted of 33.19% of nitroglycerol to 3.21 parts of nitrosaccharose, and in the black powder of 30.23 and 4.03 parts of the same ingredients respectively. Subsequent experiments appeared to show that Glukodine was merely a mechanical mixture of these ingredients as the nitroglycerol can readily be evaporated from the nitrosaccharose.

Comparatively recently,[1] C. Woodbury has patented an explosive formed of nitrated sugar 4%, nitroglycerol 30%, trinitrotoluene 10%, sodium nitrate 42%, wood meal 13% and chalk 1%, the nitrated sugar being incorporated in order to give the mixture a low freezing point.

The explosive of A. Comey[2] contains a stabilized mixture of nitrated cane sugar and trinitroglycerol.

E. Hoffmann and V. Hawse have shown[3] that nitration of sucrose in the cold by sulfuric and nitric acids yields a mixed product, and evaporation of the alcoholic solution of the latter at the ordinary temperature gives sucrose octonitrate, $C_{12}H_{14}O_3(NO_3)_8$, m. pt. 85.5°. This compound shows normal cryoscopic behavior in nitrobenzene, and no sign of decomposition when gradually heated from 33° to 87° in 2 hours. In explosive mixtures, sucrose nitrate may be estimated by means of its rotary power (+56.05° at 20°), and nitrogen content (15.95%). When purified, sucrose octonitrate appears as well-defined crystals of the orthorhombic or monoclinic systems, and is very stable.

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[1] U. S. P. 1140487, 1915; abst. C. A. 1915, **9**, 717, 2710; Chem. Ztg. 1916, **40**, 242; Mon. Sci. 1916, **83**, 73.

[2] U. S. P. 1301105, 1919; abst. J. S. C. I. 1919, **38**, 555-A; C. A. 1919, **13**, 1930. The C. Woodbury explosive (Can. P. 167827) comprizes nitrosugar, nitroglycerol and a nitro derivative of a hydrocarbon, as TNT.

[3] J. A. C. S. 1919, **41**, 235; abst. J. C. S. 1919, **116**, i, 148; C. A. 1919, **13**, 1850.

Whereas the earlier described nitrated sugars were of little practical value as explosives on account of their extreme sensitiveness and liability to spontaneous decomposition and were used but to a limited extent as a constituent of low-freezing dynamites, the recent methods of purification which have been worked out for this class of bodies, has augmented their stability to a great degree, so that at present, it would appear their field of usefulness in conjunction with other nitrated esters is of a permanent nature.

Nitrodextrin (Nitrodextrose). In 1881 G. Dean[1] described his method for the manufacture of "nitrodextrin" which was to be combined with nitroglycerol for use in blasting. He advocates bleached cotton rags as preferable for use as the raw material for the manufacture of nitrodextrin but he claims to have obtained good results by means of unbleached cotton, hemp, and wood which has been bleached. The rags are heated with dilute sulfuric, nitric, or hydrochloric acids to hydrolyze them, or with a mixture of two or more of these acids, and as the rags become tender they are removed, washed with water or weak alkaline solutions until the acid is entirely removed and then nitrated in the usual manner. The mixture of acids in nitrodextrin is drained off into water which is agitated and beaten up while the acid is falling into it, the nitrodextrin separated may then be removed and washed.

Dean's explosive comprized nitrocellulose or nitrodextrin or both 10 parts, water 2 or 3 parts and nitroglycerol 100 parts, the idea being to make the latter safer to handle and transport by forming a pasty mass in the above manner.

A. Nobel,[2] in the preparation of explosives capable of being

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[1] E. P. 2226, 1881; abst. Chem. Ind. 1881, **4**, 211. U. S. P. 242893, 1881. Can. P. 15565, 1882. F. P. 142995, 1881. Mon. Sci. 1882, **24**, 544, 730; Jahr. Chem. 1882, **35**, 1410. C. Bichel (E. P. 15528, 1885; abst. J. S. C. I. 1886, **5**, 457) has described an explosive made by distilling a hydrocarbon with sulfur, the liquid product thus obtained being combined with nitrodextrin.

[2] E. P. 6560, 1888; abst. J. S. C. I. 1888, **7**, 416. F. P. 212650, 1891.

*granulated and used in place of gunpowder, combined nitrated starch and nitrated dextrin together or separately with nitro*cellulose.

C. Lundholm and J. Sayers[1] evolved an explosive combination of nitrobenzene, nitrotoluene, nitronaphthalene and nitrophenol, together with nitrodextrin, using a mixture of camphor and acetin as the solvent or gelatinizing body.

Nitrodextrin (dextrin nitrate) is soluble in 90% alcohol.[2]

Nitroglucose. Nitroglucose has been proposed from time to time as a useful ingredient in explosive combinations but so far has proven of little, if any, commercial value due to the lack of uniformity and instability of the product.

F. Keil[3] patented a combination of nitroglucose, potassium nitrate, potassium chlorate and prepared vegetable fiber and C. Björkman[4] co-nitrated glycerol and glucose and combined the entire body thus formed with combustible bodies containing oxygen in such proportions that a powder of definite disruptive power would result, but his product seems to have found no permanent commercial application.

In the early days of the pyroxylin plastic industry when Hyatt and his co-workers on the one hand and Daniel Spill and his associates on the other were vainly endeavoring to incorporate with nitrocellulose some body or combination of bodies, either fluid or solid, to impart the desired thermoplasticity, C. Seeley[5]

The Societe Anonyme de la Poudrerie de Casteau have described (Belg. P 143691, 1899) a powder under the name of "Explosif de Casteau No. 1" composed of 1 part of resin, and 5 parts nitrodextrin.

[1] U. S P. 438816, 1890; abst. J A. C. S. 1890, **12,** 418; E. P. 6448, 1892; abst Zts. ang. Chem. 1893, **6,** 51; Wag. Jahr. 1893, **39,** 428. See also F. P. 185179, 186801; abst. Mon. Sci. 1888, **31,** 756, 883. Defraiteur, F. P. 282135, 282136, 1899; abst Mon. Sci. 1899, **53,** 187.

[2] A. Bechamp, Compt. rend. 1861, **51,** 255; Rep Chim. Pure, 1860, **2,** 478, J. Pharm Chim. 1860; **38,** 259; abst. Jahr. Chem. 1860, **13,** 521.

[3] U. S. P. 238916, 1881; abst. J. A. C. S. 1881, **3,** 67; Chem. Ind. 1881, **4,** 180. Cf. E. Bjorkman, E. P. 2459, 1875; abst. Deut. Industrie Ztg. 1876, 58; Chem Tech Rep. 1875, **14,** II, 216. U. S. P. 177988, 1876.

[4] E. P. 2483, 1880; abst. J. A. C. S. 1882, **4,** 41; Wag. Jahr. 1881, **27,** 330; Chem. Ind. 1881, **4,** 65, 207; Ber. 1881, **14,** 1426; J. S. C. I. 1882, **1,** 382. For glucose dinitrate, see E. Berl and W. Smith, J. S. C. I. 1908, **27,** 534; Chem. Zentr. 1908, **79,** II, 687. Glucose pentanitrate is described by W. Will and F. Lenze, Ber. 1898, **31,** 68.

[5] U. S. P. 79261, 1868. See also E. Worden, "Nitrocellulose Industry," 1911, **2,** 575. For industrial possibilities of nitroglucose, refer to Bonneville, F. P. 141285, 1881; abst. Mon. Sci. 1882, **24,** 730. The Commercial Research Corporation (F. P. 494441, 1917) have described explosive combinations of nitrated monoses, bioses and polyoses with polyglycols also nitrated.

made the suggestion and his idea was incorporated in patent form, that nitroglucose be used in conjunction with nitrocellulose, because the former was non-inflammable, would not turn rancid and would produce a flexible compound. While it is true that the addition of nitroglucose to nitrocellulose materially induces flexibility, the explosive nature of nitroglucose was such that no one cared to try the experiment.

"Ammonium Nitrate Powder" was also put forward as of special use for combustion purposes and comprized 80% ammonium nitrate, 5% potassium chlorate, 10% nitroglucose and 5% coal tar.

In photography de Pietteurs,[1] C. Lea[2] and others[3] endeavored to induce flexibility to collodion photographic plates by the addition of varying quantities of nitroglucose but invariably without success.

Nitrated Molasses. In 1877, under the name of Vigorite, C. Björkmann described a new explosive obtained by reacting 25–30 parts of nitric acid and 50–75 parts sulfuric acid with 5–20 parts of sugar or molasses, the nitrated product being also called by him "Nitrolin." Of this mixture 25–50 parts are incorporated with 15–35 parts of potasium nitrate, 10–30 parts potassium chlorate and 15–35 parts cellulose to make the explosive named above.[4]

The patented process of F. Gilles,[5] issued in England, likewise comprized the nitration of molasses, "nitromolasses" being obtained by nitrating 380 parts of molasses with 1,000 parts of

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In carrying their invention into effect, 40 parts of cane sugar (for instance) is dissolved in 60 parts of ethylene glycol and heated to 80°–100° to complete the solution. It is then cooled, and the mixture nitrated with 800 parts of nitrating mixture. Glucose or dextrose may also be nitrated together with glycols

[1] Bull. Soc. Franc. Phot. 1878, **24**, 256 S. Lustgarten (Monatsh. Chem. 1881, **2**, 626; Bull. Soc. Chim. 1882, **37**, 219) has described an explosive composed of glycogen nitrate (dinitroglycogen), detonating at 80°–90°. The F. Linder nitroglucose explosive, is described in Belg. P. 262118, 1913.

[2] Chem. Tech. Rep. 1868, **7**, II, 113; J. prakt. Chem. 1868, **105**, 191; Amer. Jour Sci 1868, (2), **45**, 381; Zts Chem. 1868, **11**, 532; Bull. Soc. Chim. 1868, (2), **10**, 506; Jahr. Chem. 1868, **21**, 760.

[3] Phot. Corr. 1866, **3**, 135, 162, 165, 185. Wieck's Gwz. 1867, 79. Phot. Mitth. 1878, 259.

[4] Dingl. Poly. 1877, **225**, 103; abst. Jahr. Chem. 1877, **30**, 1160. See Berg. Hütten Ztg. **38**, 123.

[5] E. P. 1883, 1883; abst. J. S. C. I. 1884, **3**, 35. D. R. P. 27969, 1883; abst. Dingl. Poly. 1885, **255**, 337; Wag. Jahr. 1884, **30**, 379; Proc. U. S. Naval Inst. 1886, **12**, 195; Tech. Chem. Jahr. 1883–4, **6**, 173.

fuming nitric acid and twice as much concentrated sulfuric acid When washed it was described as a grayish yellow or whitish precipitate.

A. Doutrelepont improved upon this process and obtained patent protection[1] in which the oxidation of the nitrated product, which was found to occur at ordinary temperatures, may, according to the patentee, be obviated by nitrating still further, the oily nitro-body described by Gilles. In this process the sugar containing material may or may not be first oxidized and the molasses obtained treated either with alcohol, ether or weak acid so that the mixed sugar containing bodies are separated, the nitrated cane sugar being separated from the nitrated molasses portion. This, according to the patentee, at best accomplished by evaporating in open evaporating dishes at 80°–90° for a few hours and until the product is reduced to the consistency of 32°–34° Bé., being then separated by crystallization. Doutrelepont combined with Schreiber in the commercial exploitation of this process under the name of Petragit, the explosive comprizing nitrated molasses 38.6%, nitrolignin 5%, potassium nitrate 56.4%. They based their claim for economical value upon the assertion that the mixture was difficultly fusible and in this distinction was superior to nitroglycerol combinations.

R. Sjöberg, under the name of "nitrolactose,"[2] patented a mixture of nitrated lactin and nitrated molasses with the subsequent addition of sodium nitrate. In the process of J. Regensburger,[3] ordinary or de-saccharinated molasses is first treated with an oxidizing substance as sodium peroxide, animal or mineral oil is then added and the mass nitrated in the usual manner.

The H. Kolf explosive[4] consists of a nitrated carbohydrate impregnated with nitrosugar, nitroglycerol and nitrotreacle.

Nitrolactose. R. Sjöberg[5] has patented a series of explosives having as a base nitrated lactose and containing, in addition, ammonium nitrate, carbonate or oxalate. The addition of naphthalene with nitrated milk sugar has also been recommended.

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[1] D R. P. 45857, abst. Wag. Jahr. 1888, **34**, 492; Jahr. Chem. 1889, **42**, 2680; Ber 1889, **22**, 156; Tech. Chem. Jahr 1888–9, **11**, 185.

[2] F. P. 192683, 1888; abst. Mon. Sci. 1889, **33**, 633. In the R. Kändler explosive (E. P. 20799, 1900; abst. J. S. C. I. 1901, **20**, 1240. India P. Appl. 414, 1901) a nitrated carbohydrate as nitrated molasses, a nitrated hydrocarbon (nitrobenzene, di-, or trinitrotoluene, di-, or trinitronaphthalene, nitrocumene) is combined with a water soluble inorganic nitrate.

[3] E. P. 4192, 1898; abst. Arms and Explos. 1899, **7**, 29; J. S. C. I. 1899, **18**, 174. D. R. P. 97289, 1898; abst. Wag. Jahr. 1898, **44**, 373; Zts. ang. Chem. 1898, **11**, 365; Chem. Centr. 1898, **69**, I, 591; Chem. Ztg. 1898, **22**, 300.

[4] E. P. 22739, 1892; abst. J. S. C. I. 1893, **12**, 1057.

[5] E. P. 448, 1887; abst. J. S. C. I. 1887, **6**, 62; Wag. Jahr. 1889, **35**,

Nitroerythrite. (Tetranitroerythrite, Butine Tetranitrate, Pentaerythrite Tetranitrate, Erythrite Tetranitrate). When the tetratomic alcohol erythrite[1] (erythrol, erythritol, mesoerythrite, erythromannite, erythroglucin, pseudorcin, eryglucin, phycite) is oxidized with dilute nitric acid, oxalic and tartaric acids[2] and an aldehyde or ketone,[3] or at least a body which reduces Fehling's solution[4] is formed.

It was J. Stenhouse who first noticed[5] that upon dissolving small quantities at a time of powdered erythrite in fuming nitric acid, keeping the solution cool and mixing it with an amount of sulfuric acid equal to or greater than the nitric acid, a crystalline mass is obtained, which, when washed with water to neutrality, gave large crystalline plates of nitroerythrite melting at 61° and solidifying in the crystalline form at a temperature a few degrees lower.

The method of B. Thieme for the preparation of this compound is to produce pentaerythrite from the condensation of acetaldehyde and formaldehyde in the presence of lime. By fusing between 190°-260°, the powdered melt when dissolved in

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478 E P 11658, 1887; abst J S. C. I. 1887, **6,** 760 F P. 192683; abst. Mon Sci. 1889, **33,** 633

1 J Stenhouse, Phil Trans. 1848, **138,** 76; 1849, **139,** 399; abst. Ann 1848, **68,** 78; 1849, **70,** 225. A. Strecker, Ann. 1848, **68,** 111. E. Schunck, Phil. Mag. 1854, **7,** 33, 254. A. Lamy, Ann Chim. Phys. 1852, **35,** 138, 1857, **51,** 232, abst N. J. Pharm. **22,** 43, Ann. 1852, **84,** 369; J. prakt. Chem. 1852, **57,** 21; Chem. Centr. 1853, **24,** 302. R. Wagner, J. prakt. Chem. 1854, **61,** 125. B. Merejkowsky (D. R. Anm. M-50150) prepares pentaerythrite by condensing formaldehyde and acetaldehyde in the presence of lime.

2. S. Przybytek, Bull. Soc Chim, 1881, (2), **35,** 108; abst. J. C. S. 1881, **40,** 402; Ber. 1881, **14,** 2072; Jahr. Chem. 1881, **34,** 514.

3. E. Fischer and J. Tafel, Ber. 1887, **20,** 1088; abst. J. C. S. 1888, **39,** 358, 484; Bull. Soc. Chim. 1888, **49,** 359, 972; Jahr. Chem. 1887, 1282.

4. For accidents attending the use of nitroerythrite see A. Dupre, Ann. Rept. H. M. Inspectors of Explosives, 1897, 27; A. Ford, Ann. Rept. H M. Inspectors Explosives, 1899, 145; abst. J. S. C. I 1899, **18,** 415. For lead-block tests with pentanitroerythrol prepared according to D. R. P. 265025 of C. Claessen; abst. C. A. 1914, **8,** 251; see Sprengst. Waffen Mun. 1914, **9,** 29; abst. C. A. 1915, **9,** 1392.

5. Trans. Roy. Soc. Lon. 1849, **139,** 399; abst. J. prakt. Chem. 1864, **92,** 332; Ann. 1849, **70,** 226; 1864, **130,** 302. J. C. S. 1849, **16,** 399; Jahr. Chem. 1849, 460; Chem. Centr. 1849, **20,** 627.

nitric acid and precipitated by sulfuric acid forms a crystalline product insoluble in cold water, melts when heated in a flame, but burns away quietly unless confined. It is advocated as an explosive, either alone in a dry state, or in conjunction with nitrocellulose, with which it may be intimately incorporated by means of a fluid which is a solvent of both, such as ethyl acetate.[1] The Rheinisch-Westphalische Sprengstoff A.-G.[2] have patented the use of nitroerythrite for regulating the combustion and inflammability of nitrocellulose smokeless powders. It is a fact that to increase the ballistic effect of nitrocellulose or nitrostarch powders, the particles or individual grains must be as large as possible, while on account of the gas pressure they must be as thick as possible. Both are only possible to a limited degree, as otherwise the explosibility and inflammability would be seriously affected. The addition of small amounts of nitroerythrite is claimed to remove this drawback in a large measure, in that it causes a very uniform burning of the powder containing it.

In the manufacture of detonating compositions, C. Claessen[3] adds nitroerythrite to such explosives as tetranitromethylaniline, tetranitroethylaniline, nitrotoluene, trinitrophenol and lead azide, a suitable composition being given as nitroerythrite 1 part, lead azide 0.2 part; or[1] picric acid and trinitrotoluene may be added to nitropentaerythrite in conjunction with a small layer of mercury fulminate to initiate the explosion. Similarly[2] E. Herz adds preferably about 15 parts of this body to ammonium nitrate combinations in order to produce easily detonating safety explosives of great density which at the same time are safe against fire damp. A diazoperchlorate of a nitrated aromatic hydrocarbon, such as nitrodiazotolueneperchlorate, may or may not be present.[3] The patented process of J. Harlé[4] consists in the use of tetranitropentaerythrite alone or mixed with nitrobenzene, nitrotoluene, nitrophenol or nitrated amines in string-like detonating fuses.

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[1] E. P. 20281, 1894; abst. J. S. C. I. 1895, **14,** 66; U. S. P. 541899, 1895.

[2] D. R. P 81664, 1895; abst. Chem Tech Rep 1895, **34,** II, 267; Jahr. Chem. 1895, **48,** 1002; Wag Jahr. 1895, **41,** 459; Ber. 1895, **28,** 827; Zts. ang. Chem. 1895, **8,** 388. F. P. 242847, 1895. In a recent process of this firm (D. R. P. 298932, 1914; abst J. S C. I 1920, **39,** 385-A; Chem Zentr. 1920, **91,** II, 338) in the working up of crude pentaerythrite solutions, the calcium formate is separated from the hot concentrated crude solution, and the pentaerythrite allowed to crystallize out in the cold. The solubility of the pentaerythrite increases considerably with increase in temperature, whereas that of the calcium formate is practically unchanged The crude solution may be advantageously neutralized prior to evaporation

[3] F. P. 451925; abst. C. A. 1913, **7,** 3843; Chem. Ztg. Rep 1913, **37,** 478; Mon Sci. 1914, **81,** 51. U S. P. 1240236; abst. C. A. 1917, **11,** 32. U. S. P. 1254147; abst. C. A. 1918, **12,** 766; J. S. C. I. 1918, **37,** 224-A. Swed. P. 40749, 1916; abst. C. A. 1916, **10,** 2525. Swiss P. 61926, 1912. Aust. P. 64976, 1913. D. R. P. 166804; abst. Zts. ang. Chem. 1906, **19,** 253; Chem. Centr. 1906, **77,** II, 626; Wag. Jahr. 1906, **52,** I, 486; Mon. Sci. 1907, **67,** 107. D. R. P. 168490; abst. Zts. ang. Chem. 1906, **19,** 253; Chem. Centr. 1906, **77,** I, 1471; Chem. Ztg. 1906, **30,** 277; Wag. Jahr. 1906, **52,** I, 486; Mon. Sci. 1908, **69,** 47; Zts. Schiess. Spreng. 1906, **1,** 103. D. R. P. 265025; abst. C. A. 1914, **8,** 251; Zts. ang. Chem. 1913, **26,** 749; Chem. Zentr. 1913, **84,** II, 1445; Chem. Ztg. Rep. 1913, **37,** 572; Wag. Jahr. 1913, **59,** I, 447; Zts. Schiess. Spreng. 1913, **8,** 397. Can. P. 176609, 1917; abst. C. A. 1918, **12,** 226.

In the C. Claessen process, finely powdered pentaerythritol is introduced slowly and with continual stirring, into a large excess of 96% nitric acid. If the temperature rises above 30° during the process of nitration the reaction mass is cooled with water, while the addition of the pentaerythrol is temporarily discontinued until the temperature of the nitrating bath has fallen below 30°. After the desired amount of the erythrol has been added concentrated sulfuric acid is introduced in great excess, whereby the nitropentaerythrol, which is present in greatest amounts in the nitric acid, is precipitated almost quantitatively. The resulting nitroproduct is separated from the acid and washed with cold water to neutrality. The neutral product is then dried at a low temperature and recrystallized from acetone. The nitrogen content is 17.72%.

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[1] E. P. 29901, 1912; abst. J. S. C. I. 1913, **32**, 886; C. A. 1914, **8**, 2062. F. P. 451925; abst. J. S. C. I. 1913, **32**, 674; C. A. 1913, **7**, 3843; Chem. Ztg. Rep. 1913, **37**, 478; Mon. Sci. 1914, **81**, 51. E. P. 13086, 1913; abst. C. A. 1914, **8**, 3860; J. S. C. I. 1914, **33**, 222. F. P. 459979; abst. C. A. 1914, **8**, 3238. Swiss P. 64712, 1913. D. R. P. 281497; abst. Zts. ang. Chem. 1915, **28**, II, 126; Chem. Ztg. Rep. 1915, **39**, 42; Wag. Jahr. 1915, **61**, I, 279.

[2] E. P. 11809, 1913; abst. J. S. C. I. 1914, **33**, 44; C. A. 1914, **8**, 3537. In one example cited, 73.6% ammonium nitrate, 12.6% pentaerythrite tetranitrate, 7.8% trinitrotoluene and 6% potassium nitrate is recommended as especially efficient. In Spreng. Waff. u. Munition, 1914, **9**, 29; abst. C. A. 1915, **9**, 1392, are described lead-block tests with pentanitroerythrol prepared according to D. R. P. 265025. Using a detonator alone containing 1 gm. with 0.2 gm. lead nitride, priming, there was obtained an expansion measuring 46 cc. in a lead block having a hole measuring 10 × 10 cm. originally. A detonator having a charge of 1 gm. tetranitromethylaniline with 0.2 gm. lead azide gave 34.5 cc. expansion, while 1 gm. TNT with 0.2 gm. lead azide, gave but 29.5 cc. In trials with explosives hard to detonate, the results with pentanitroerythrol were also satisfactory.

[3] U. S. P. 1054411; abst. C. A. 1913, **7**, 1419. E. P. 27198, 1912; abst. C. A. 1914, **8**, 1672; J. S. C. I. 1913, **32**, 713. F. P. 450897; abst. J. S. C. I. 1913, **32**, 627; Mon. Sci. 1914, **81**, 51.

[4] E. P. 15355, 1914; abst. C. A. 1916, **10**, 119. F. P. 471164, 1914. U. S. P. 1306895, 1919; abst. C. A. 1919, **13**, 2283. In the cap composition of the Canadian Explosives Co. (Can. P. 176609) the initial igniter contains nitropentaerythrite.

Nitroerythrite deposits in large colorless plates (from alcohol) which are insoluble in cold water; slightly more soluble in hot water; readily soluble in alcohol, ether, chloroform, ethyl acetate and amyl acetate; almost insoluble in carbon tetrachloride, acetylene tetrachloride, amyl alcohol, pyridine, quinoline, benzene, toluene and xylene. It is highly sensitive and explodes easily when struck. Its sensibility to percussion is greater than that of dynamite or guncotton. Alcoholic ammonium sulfide reconverts it into erythrite. It contains 17.72% N. Nitropentaerythrites, in addition to their possibilities as explosives as a substitute for or in conjunction with the fulminates, have come into some use in place of nitroglycerol as a remedy for angina pectoris.[1]

The nitropentaerythrite produced in conformity with the process patented by Thieme previously described, possesses the quality of melting when heated in a flame and will then burn away steadily without explosion, and owing to this quality the patentee asserts the uniformity of combustion in other explosives can be modified within well defined limits by the addition thereto of nitropentaerythrite. Erythronitrate has a composition $C_4H_4(NO_3)_4$ and contains one oxygen less than is necessary for complete combustion of the carbon and hydrogen, but the excess is less than in nitroglycerol. In its behavior to heat it resembles somewhat picric acid. It is not very sensitive to friction, can scarcely be exploded by a glancing blow with a wooden mallet, even on stone. On the other hand it is extremely sensitive to percussion and can be exploded with the greatest ease in a porcelain mortar with a porcelain pestle. It is related that during the mixture of a small amount of this compound with its own weight of sugar of milk in a porcelain mortar, an explosion happened which killed one man.

The application of heat to pentaerythritolformate produces the calculated quantity of carbon monoxide and regenerates pentaerythritol.[1] An erythrodinitrodichlorhydrin, erythrodinitrodibromhydrin and an erythrodibromhydrin are known.[2]

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[1] J. S. C. I. 1899, **18**, 415. The process of Friederich (E. P. 138083, 1920; abst. C. A. 1920, **14**, 1758) consists in the use of lead trinitroresorcinate above a layer of lead azide over a detonator charge of nitropentaerythrite and tetranitromethylaniline.

A. Stettbacher[3] has thoroughly investigated pentanitroerythrol and has found that on nitration a compound is produced which combines the explosive properties of nitromannitol and nitroglycerol, while being free from the majority of the disadvantages of these. Their procedure for the preparation of pentaerythritol in detail is as follows: The materials are mixed in a wooden vat, of 110 liters capacity, according to the relation given by Tollens and Wigand; 1940 gm. formaldehyde, 600 gm. acetic acid, 90 liters of water and 1600 gm. slaked lime. The charging of the tank is as follows: First 85 liters of water, then 5 liters of milk of lime containing 1100 gm. calcium hydroxide, and finally the formaldehyde and acetic acid in the quantities above given. The bung hole is closed tightly and the tank is rolled three times a day for three weeks. It is then allowed to remain at rest for a day or so more and the clear solution then filtered off. The lime and calcium formate in solution with the pentaerythritol are removed by adding 140 gm. pulverized oxalic acid in crystals and filtering off the calcium oxalate. The free formic acid changes

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1. P van Romburgh, Proc Acad Amsterdam, 1909, **10**, 166; abst. J C S 1907, **92**, i, 1011, C. A. 1909, **3**, 169. According to H. M Inspector of Explosives, 1897, p. 27, erythroltetranitrate has recently come into use in place of nitroglycerol as a remedy in angina pectoris. They record that it is a crystalline solid, m pt 158° F., and when suddenly heated to a high temperature explodes with great violence. In its behavior to heat it somewhat resembles picric acid. It is not very sensitive to friction and can scarcely be exploded by a glancing blow with a wooden mallet, even on stone. On the other hand, it is extremely sensitive to percussion, and can be exploded with the greatest ease in a porcelain mortar by means of a porcelain pestle.

2. P. Champion, Zts. Chem. 1871, **7**, 348, 349; abst. J C. S. 1871, **24**, 811; Compt. rend. 1871, **73**, 114; Jahr. Chem. 1871, **24**, 417; Bull. Soc. Chim. 1871, **16**, 301.

3 Zts. Schiess. Spreng. 1916, **11**, 182; abst J. S C. I 1917, **36**, 101; C. A 1917, **11**, 2543. See also E. P. 20281, 1894; abst. J. S C. I. 1895, **14**, 66. According to L. Vignon and I. Bay (Compt. rend. 1902, **135**, 507; abst. J. S. C. I 1902, **21**, 1303) the reducing action on Fehling's solution shown by the nitric esters of erythritol, mannitol, dulcitol, pentaerythritol, etc., is accompanied by, and is, no doubt, correlated with, the saponification of the esters by the alkali of the Fehling's solution. The authors, have investigated the conditions of saponification by water, by acid, and by alkali of the nitric esters of the alcohols named together with those of methyl alcohol, ethyl alcohol, and glycerol. In the case of water, there is no saponification in any instance, either on heating on the water bath, or on boiling at atmospheric pressure; but in a sealed tube at 110°-120°, the esters of the 4-, 5- and 6-carbon alcohols are completely saponified.

the clear solution to a bright yellow. This solution is then evaporated to one-tenth to one-twelfth its original volume, preferably in a vacuum still. The brown residue, after cooling, is filtered, the pentaerythritol which remains on the filter having a melting point of 235 to 240 degrees. A tank yields about 1200 gm. of raw product. This raw product is powdered and rubbed with a small quantity of strong ethyl alcohol, then dried and finally recrystallized from water. The pulverized pentaerythritol is stirred with an excess of concentrated nitric acid, the latter being added slowly so that the temperature is not allowed to rise above 30°. After all of the acid is added an excess of concentrated sulfuric acid is poured in, when the conversion into pentaerythritol nitrate is almost quantitative. The product is washed free from acid by water and then crystallized from acetone. The pentaerythritol tetranitrate thus obtained is claimed to be stable and unchanged after heating for two hours at 80°.

Nitromannite (Nitromannitol, Fulminating Mannite, Fulmin Mannite, Pentanitromannitol, *a*-Hexone-hexanitrate, Hexanitrin). Mannite or sugar of manna, discovered by J. Proust,[1]

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[1] Ann. Chim. Phys. 1806, (1), **57**, 143; J. de Phys. 1806, **57**, 143; Gehlen J. 1806, **2**, 77, 376, 420; Gilb. Ann. Phys. 1803, **15**, 296; Nicholson's J. 1808, **21**, 306, 341. See also J. Liebig and J. Pelouze, Ann. 1836, **19**, 263. P. Favre, Ann. Chim. Phys. 1844, (3), **11**, 71; Berz. Jahr. 1846, **25**, 561; J. prakt. Chem. 1844, **32**, 362; Ann. 1844, **52**, 310.

Many carbohydrates like mannite might prove to be exceedingly valuable explosive bodies when nitrated and be used in immense quantities, but their use at present is precluded on account of the high cost of the carbohydrate. Recently extensive experiments have been undertaken to obtain these bodies cheaply in large amounts, and with some degree of success. Mannite is found in considerable amounts in the liquor from silage, being especially high in silage made from sunflower stalks, which contain about 5% of mannite on the wet basis. The method of extraction is to add alcohol to the concentrated liquor, whereupon mannite crystallizes out. P. Maze (Ann. Inst. Pasteur, Sept. 1903; Ann. de la Brasserie, 1903, **6**, 442; J. S. C. I. 1903, **22**, 1361) produces mannitol by deleterious ferments in wines. The General Electric Co. (E. P. 24060, 1912; abst. J. S. C. I. 1913, **32**, 951) produce plastics from mannite, resins, camphoric acid, and the condensation product of glycerol and phthalic acid.

C. Hudson and H. Sawyer (Jour. Amer. Chem. Soc. 1917, **39**, 470; abst. J. S. C. I. 1917, **36**, 467) have described a method for the preparation of mannose from vegetable ivory (from seeds of the tagua palm, *Phytelephas macrocarpa*), in which the material is hydrolyzed with sulfuric acid, and a yield of 30%–35% of the crystallized sugar is obtained without intermediate conversion into phenylhydrazone. The mutarotation of mannose is a unimolecular reaction. Its velocity constant increases about 2.6-fold for a rise in temperature of 10°, and is independent of concentration below 10%, but increases above to a maximum at 45 gm. per 100 cc. and decreases again beyond. Like that of dextrose, the mutarotation of mannose is accelerated by acids, and to a much greater extent by alkalis. It is doubtless due to a exists in many vegetables, but is usually prepared from manna and saccharine juice obtained from two specie of ash. It occurs to the extent of 30 to 60 per cent. in manna, the dry juice which exudes from the manna ash (Fraxinus ornus).[1] When mannite is oxidized with nitric acid[2] it is converted into saccharic acid and not mucic acid, but upon pushing the oxidation further oxalic acid is obtained. A commercial method for the preparation of mannite has been recently patented by G. Guignard.[3]

This ester has been investigated by F. Flores-Domonte and Menard,[4] A. Sobrero,[5] J. Stenhouse,[6] L. Svanberg and Staaf,[7] and A. Knop,[8] the general method of preparation being to dissolve one part of mannite in two parts by weight of cooled fuming nitric acid, then adding sulfuric acid until no more white flakes are precipitated, when the mass is at once poured into water, purification being effected by boiling in alcohol. A. Sobrero, observing the powerful explosive effect of nitromannite on percussion endeavored to replace mercury fulminate by this explosive in percussion caps. S. deLuca,[9] H. Reinsch,[10] V. Dessaignes,[11]

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balanced action between α- and β-forms. Crystallized mannose is generally assumed to be the β-form.

[1] See A. Payen, Ann. Chim. Phys. 1833, **55**, 219, Ann 1834, **12**, 60. W. Meyer and von Reiche, Ann. 1843, **47**, 234.

[2] Watt, Dict. Chim. 1875, **3**, 824.

[3] E. P. 3261, 1913; abst. C. A. 1914, **8**, 2595, J S. C. I. 1913, **2**, 879; Chem. Ztg. Rep. 1914, **38**, 538.

[4] Compt. rend. 1847, **24**, 89, 390; N. J. Pharm. (3), **12**, 159; Pharm. Centr. 1847, **18**, 892; Jahr. Chem. 1847-8, **1**, 1145, Ann. Rep. Chem. 1847-8, 377.

[5] Ann. 1845, **64**, 397; abst. Jahr. Chem. 1847-8, **1**, 1145; Amer. J. Sci. 1847, **4**, 274; Compt. rend. 1847, **24**, 247; **25**, 121; Dingl. Poly. 1847, **105**, 387; Ann. Rep. Chem. 1847-8, **1**, 377; J. prakt. Chem. 1847, **40**, 421; Berz. Jahr. 1849, **28**, 358; Rev. d'Artil. 1877, **9**, 297.

[6] Ann. 1846, **60**, 218; Chem. Centr. 1849, **20**, 625; Chem. Gaz. 1849, 265; Phil. Mag. 1849, **34**, 463; Instit. 1849, 268; Jahr. Chem. 1849, **2**, 466.

[7] Skand. Naturf. Förhandl. 1847, **5**, 337; Oversigt, 1847, **4**, 214; abst. Berz. Jahr. 1849, **28**, 360. See also F. Uchatius, Dingl. Poly. 1861, **161**, 146; abst. Poly. Centr. 1861, **27**, 1367; Poly. Notizbl. 1861, **16**, 309. For the nitromannite of E. Mills, see J. C. S. 1864, **17**, 153; 1865, **18**, 319; Chem. News, 1864, **9**, 162; abst. Bull. Soc. Chim 1865, **4**, 280; J. Pharm. Chim. 1866, **3**, 99; Chem. Centr. 1866, **37**, 229; Jahr. Chem. 1864, **17**, 584; Zts. Chem. 1864, **7**, 282.

[8] J. prakt. Chem. 1849, **48**, 362; 1850, **49**, 228; Ann. 1850, **74**, 347; abst. Chem. Centr. 1849, **20**, 801; 1850, **21**, 49; Jahr. Chem. 1849, **2**, 466; Chem. Gaz. 1850, 81.

[9] Amer. Drug. Circ. Feb. 1866; Amer. J. Pharm. 1866, **38**, 179; Compt. rend. 1861, **53**, 298; Dingl. Poly. 1861, **162**, 137; Poly. Centr. 1862, **28**, 221; Wag. Jahr. 1861, **7**, 517; Inst. 1861, 275; J. prakt. Chem. 1862, **85**, 378; J. Pharm. Chim. 1862, **41**, 483; Jahr. Chem. 1861, **14**, 713.

[10] Jahr. Pharm. **18**, 102; Repert. Pharm. (3), **3**, 6; Pharm. Centr.

A. and W. Knop[1] and M. Berthelot,[2] especially the latter, observed that nitromannite exists in several modifications in which he was able to chemically distinguish between the compound of L. Svanberg and Staaf[3] and that of A. Strecker,[4] and confirms the observation previously made that by the action of ferrous acetate upon nitromannite, unaltered mannite may be recovered together with a substance similar to or identical with mannitan. T. Tichanowitsch[5] communicated further details on the decomposition products of nitromannite by ammonia. The pure product used by him melted at 72°, had a dextro rotation of 48.8, was soluble at 12.8° in 34.4 parts of alcohol of sp. gr. 0.81; and at 9° in 24.4 parts of ether, and was decomposed when dry at a temperature of 120°, and when containing small amounts of moisture, at 100° or under.

According to N. Sokoloff[6] nitromannite may be readily prepared by rubbing up one part of mannite in five parts by weight of cooled nitric acid of sp. gr. 1.5, the solution then being poured into a well cooled vessel and mixed with ten parts of sulfuric acid. The semi-solid mass resulting is filtered and the residue well washed with water and finally with dilute soda solution to substantial neutrality. To obtain the nitromannite in a pure state it must be repeatedly crystallized from alcohol when it then consists of long, white needles melting at 112° to 113°, which, however, are decomposed at a higher temperature. The sp. gr. of the crystals at zero is 1.604 and of the fused product, 1.446 to

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1849, 506; Jahr. Chem 1849, **2**, 469; Berz. Jahr. Chem. 1851, **30**, 371; Arch. Pharm. **18**, 271; J. prakt Chem. 1849, **47**, 477, Poly. Centr. 1849, **15**, 1467; Dingl. Poly. 1849, **114**, 432.

[11] Compt. rend. 1851, **33**, 462; Instit 1851, 347; Ann. 1852, **81**, 251; J. prakt. Chem. 1852, **55**, 33; abst. Jahr. Chem. 1851, **4**, 552.

[1] Pharm. Centr 1852, 129, 423; J. prakt. Chem. 1849, **48**, 362; 1850, **56**, 334; abst. Jahr. Chem. 1852, **5**, 657; Chem. Gaz. 1850, 81; Ann. 1850, **74**, 347.

[2] Compt. rend. 1855, **42**, 1111; Instit. 1856, 205; Arch. ph. Nat. **32**, 333; J. prakt. Chem. 1856, **69**, 450; Chem. Centr. 1856, **27**, 625, Jahr. Chem. 1856, **9**, 662.

[3] Jahr. Chem. 1856, **9**, 662.

[4] Jahr. Chem. 1856, **9**, 662; Ann. 1850, **73**, 59; **74**, 347; Ann. Rep. Chem. 1849, **3**, 323; Chem. Gaz. 1850, 149.

[5] Zts. Chem. 1863, **6**, 550; 1864, **7**, 482; abst. Jahr. Chem. 1863, **16**, 584; 1864, **17**, 582; Chem. Centr. 1864, **35**, 463.

[6] Ber. 1879, **12**, 688, 698; J. C. S. 1879, **36**, 777, 1080; Bull. Soc. Chim. 1880, **33**, 165; Jahr. Chem. 1880, **33**, 1026; Chem. Tech. Rep. 1879, **18**, I, 286; Year Book Pharm. 1880, 80; Gewerbebl. **12**, 688, 698; Pharm. Centralh. 1879, **20**, 277; Chem. Centr. 1879, **50**, 374; Wag. Jahr. 1879, **25**, 423.

1.537. In contact with a glowing wire or a gas flame nitromannite melts but does not burn. When thrown on glowing coals it first melts, then violently explodes. However, it may be pressed and rubbed up in a porcelain mortar without danger, or cut or sawed. When pressed under the blow of a hammer, however, it is claimed to explode more violently than mercury fulminate, and also detonates by the action of ferrous fulminates. Nitromannite pressed into a metal capsule explodes by the action of fulminates only when a certain quantity of the powdered compound is also present. Contained loosely in capsules not sealed up, it explodes only by the action of diazobenzene nitrate. Sokoloff claims that the explosion of nitromannite is produced only by certain determinate vibrations.

J. Wigner,[1] who has more recently investigated the nitrates of mannitol and of dulcitol, claims, that in distinction to the results published by Tichanowitsch,[2] dulcitol hexanitrate is not decomposed by prolonged heating at 40°, and mannitol hexanitrate, whether wet or dry, is only very slowly decomposed at 100°, the melting point falling one degree in fifteen minutes and four degrees in forty-five minutes. His preferred method for the preparation of mannitol pentanitrates is by direct nitration of mannitol, but the pentanitrate is also mixed with the hexa derivative, separation from which may be effected by diluting the nitration mixtures until most of the hexanitrate is precipitated, then evaporating and again diluting. His preferred method of preparing the pentanitrate, however, is by dissolving the hexanitrate in alcohol, adding pyridine[1] and boiling for an hour, the pyridine being removed by pouring into water, and extracting the water with ether. The product when then recrystallized, melts at 81° to 82°[2] and dissolves in 3,000 parts of water at 15°, has a normal molecular weight and recrystallizes unchanged from acetyl chloride.[3] Nitromannite is claimed to be more susceptible to friction than nitroglycerol, and unless pure is liable to spontaneous combustion. Chemically it is the nitric ester of the hexatomic alcohol mannitol. L. Vignon and F. Gerin[4] have found that pentanitromannitol and hexanitromannitol obtained by the action of sulfuric and nitric acids on mannitol, readily reduce Fehling's solution and in this respect resemble the nitrocelluloses.[5] They do not react upon Schiff's reagent however, and in this respect differ from the cellulose nitrates. A further distinction is found in the fact that whereas nitrocellulose gives oxy-cellulose when treated with ferrous chloride, the nitromannitols yield mannitol, which has no reducing power. The cupric reducing power of mannitol is greater than that of dextrose but is not due to the presence of mannose. F. Krecke,[6] as the result of his investigation upon mannite and nitromannite found:

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[1] Ber. 1903, **36**, 794; abst J C S. 1903, **84**, i, 394; Bull Soc. Chim. 1903, **30**, 1174; Chem. Centr. 1903, **74**, I, 596; Jahr. Chem. 1903, **56**, 767; Meyer Jahr. Chem. 1903, **13**, 345.

C. Marshall and J. Wigner (Chem News, 1902, **85**, 103; Proc. Chem. Soc. 1902, **18**, 32; abst. Chem. Centr. 1903, **74**, I, 628; Jahr. Chem. 1902, **55**, 806) have criticized the theory advanced by Vignon and Gerin concerning the constitution of hexanitromannite and related substances. According to these authors such higher nitrates are supposed to reduce Fehling's solution, while the lower nitrates, for example nitroglycerol, do not do so. They assume the CH_2OH radical is changed during the nitration into a hydrated aldehyde group $CH(OH)_2$, which is changed under the action of the N_2O_3 into a CH(OH)ONO group and that by the action of the alkali from the Fehling solution this group is alleged to result in the formation of aldehydic groups. The authors further advance the argument that the amount of N_2O_3 that is formed during the hydrolysis would materially change the different members of the series, which is not the case. These authors are unable to agree that the above mentioned compounds are nitric acid esters of modified alcohol.

[2] Zts. Chem. 1864, **7**, 482; abst. Jahr. Chem. 1864, **17**, 582; Chem. Centr. 1864, **35**, 463.

1. Optically active mannite is transformed under the influence of a mixture of $HNO_3.H_2SO_4$ into active nitromannite.

2. Optically active nitromannite is transformed by the

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[1] In place of the ammonia used by T.

[2] Tichanowitsch gave 79°.

[3] Dulcitol pentanitrate, prepared by a similar method and re-crystallized three times from alcohol and water, sinters at 71° and melts at 75°, and like mannitol pentanitrate it has a bitter taste and strong physiological action. According to F. Homann (Ann. 1878, **190**, 282; J. C. S. 1878, **34**, 399) by the action of a mixture of one part of concentrated nitric acid and ten parts of sulfuric acid, quercite pentanitrate, is obtained which is an almost colorless resinous mass, insoluble in water, but readily soluble in absolute alcohol and in ether. It explodes on heating. Quercite is not altered by heating with concentrated hydrochloric acid under pressure at 100°.

[4] Compt. rend. 1901, **133**, 515, 540; J. C. S. 1901, **82**, i, 662; Jahr. Chem. 1901, **54**, 651, 652; J. S. C. I. 1901, **20**, 1244; Bull. Soc. Chim. 1902, **27**, 24; Chem Centr. 1901, **72**, II, 983; 1902, **73**, I, 456. See Chem. News, 1901, **84**, 202.

[5] L. Vignon, Compt. rend. 1900, **131**, 509, 530, 558; abst. J. C. S. 1900, **80**, i, 589, 628. L. Vignon and J. Bay, Compt. rend. 1902, **135**, 507; abst. Jahr. Chem. 1902, **55**, 805.

[6] Arch. neerland. 1872, **7**, 202; abst. Jahr. Chem. 1872, **25**, 155. For the decomposition of nitromannite, see E. Sarrau and P. Vieille, Compt. rend. 1881, **93**, 269; abst. Wag. Jahr. 1881, **27**, 341; Chem. Ind. 1881, **4**, 384; Chem. Tech. Rep. 1881, **20**, II, 134; J. C. S. 1881, **40**, 1033; Jahr. Chem. 1881, **34**, 1131; Zts. physik. Chem. 1889, **3**, 153.

action of ammonium sulfite into inactive nitromannite with reduction.

3. The active grape sugar is transformed by sodium or potassium amalgams into inactive mannite.

4. The mannite obtained in this manner is transformed into active nitromannite by the same treatment as that obtained from manna sugar.

According to A. Loir[1] the nitromannites are always dextrogyrate. M. Berthelot[2] prepared nitromannite by the action of nitro-sulfuric acid upon carefully purified mannite; the reaction was slow and lasted considerable time. Admitting an entire conversion, the number obtained gave 21,200 heat units for the reaction

$$C_6H_{14}O_6 + 6NO_3H = C_6H_8(NO_3)_6 + 6H_2O,$$

or 3500 per equivalent of acid fixed.

In 1880, J. Engels[3] obtained protection for a dynamite of high blasting and expanding quality, made of a combination of pyroxylin, nitroglycerol, "pyro paper," "nitro amylin" and nitromannite, either with or without small amounts of potassium silicate. Amark's explosive[4] is said to include nitroglycerol and nitromannite or nitro-starch, together with infusorial earth, but usually with a small quantity of flour or resin. A. Nobel obtained patent protection in 1893[5] for an explosive compound wherein nitromannite, with or without the addition of substances as dinitrobenzene, mononitrobenzene, trinitrobenzene, dinitrotoluene, and trinitrotoluene, is used as a solvent for nitrocellulose. The advantage claimed for nitromannite in this respect over nitroglycerol consists in the fact that it is at ordinary temperatures a solid substance and therefore unlike nitroglycerol not subject to the possibility of exudation. In the preferred method of procedure, 20 parts by weight of nitromannite and 20 parts of dinitrobenzene are melted together on the water bath, in which condition they are easily incorporated with 60 parts of nitrocellulose, a substance of great consistency and excellent ballistic qualities, according to the patentee, being thus obtained. Furthermore, the patent specification states, it is unnecessary that all the nitrocellulose contained therein should be dissolved, it sufficing that only such part be dissolved as to give the requisite consistency, whereas the remaining part may be imbedded undissolved in the plastic material without the development of deleterious reaction. The process of F. von Schaller[1] is somewhat similar, insoluble nitrocellulose being incorporated with a mixture of trinitrotoluene, nitromannite or nitroglycerol, and heated in the presence of benzene to 60° or 70°, with or without the addition of vaseline, oil or paraffin. The solution is then precipitated by water, washed, dried and formed in the usual manner. Xyloglodine is alleged to consist of glycerol and starch or glycerol and cellulose or glycerol and mannite, or benzene jointly nitrated with the usual acid mixture. It is claimed for this product (upon what grounds is not stated) that it differs in certain important characteristics from a mixture of the two compounds nitrated separately and then combined. A. Smolka[2] has described mannitol lead nitrate as a desirable explosive body.

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[1] Bull Soc Chim. 1861, **12**, 113, abst Jahr Chem. 1861, **14**, 729; Proc. Amer Pharm Assoc 1863, **11**, 145, Chem. Centr. 1863, **34**, 159.

[2] Compt rend 1871, **73**, 260, abst J. C. S. 1871, **24**, 872; Jahr. Chem. 1871, **24**, 81, Bull Soc Chim. 1871, **16**, 223; Zts Chem. 1871, **14**, 345.

[3] E. P. 163, 1880; abst J A C. S. 1880, **2**, 405. D. R. P. 10232, 1879; abst. J A. C S. 1880, **2**, 405; Ber. 1880, **13**, 1765; Chem. Ind. 1880, **3**, 276; Industriebl 1880, 339, Chem. Tech Rep 1880, **19**, I, 339; Deut. Industrieztg. 1880, 401; Chem Ztg. 1880, **4**, 522, 733; Jahr. Chem. 1880, **33**, 1311.

[4] Chem. Tech. Ztg. 1887 E. Votocek and C. Kranz (Zts. Zuckerind. 1919, **43**, 577; abst C A. 1920, **14**, 1674) find that aqueous solutions of mannitol are slowly oxidized by nitrous fumes, yielding a mixture of mannose and levulose, and that the reaction can be accelerated by the addition of small quantities of a ferrous salt. Nitrous fumes in this case behave like other oxidizing agents, yielding a mixture of aldehydic and ketonic products.

[5] E. P. 11645, 1893; abst. J. S. C. I. 1894, **13**, 760; Arms and Explos. 1894, **2**, 203. According to E. P. 12742, 12743, 12744, 12745, 12746, 1912 (abst. C. A. 1913, **7**, 3842; J. S. C. I. 1913, **32**, 991; Chem. Ztg. Rep. 1913, **37**, 614) granted to F. Nathan, W. Rintoul and T. Baker, processes are described wherein there is added to explosives containing nitrocellulose, nitromannite, nitrostarch and nitroglycerol, substances such as simple or mixed esters, containing at least one aromatic radical capable of ready nitration by the products of decomposition of nitro-explosives, have no deleterious effect on the explosive and capable of being homogeneously retained in the explosive

Hexanitromannite is a crystalline solid, sensitive to shock, insoluble in water, but readily soluble in alcohol, ether, chloro-

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in sufficient quantities for effective stabilization. Diphenyl ether, phenylbenzyl ether, ethyl-naphthyl ether, phenanthrylmethyl ether, ethyl-phenyl urea, and esters of substituted carbaminic ether with or without one or more radicals instead of the customary addition of vaseline or mineral jelly.

[1] D. R. P. 141314; abst. Zts. ang. Chem. 1903, **16**, 634; Jahr. Chem. 1903, **56**, 1018; Chem. Ztg. 1903, **27**, 600; Wag. Jahr. 1903, **49**, I, 343; Chem. Zts. 1904, **3**, 14.

[2] Monatsh. 1885, **6**, 198; abst. J. C. S. 1885, **48**, 743; Proc. U. S. Naval Inst. 1886, **12**, 189; Ber. 1885, **18**, 330-R; Jahr. Chem. 1885, **38**, 1209; Bull. Soc. Chim. 1886, **45**, 753.

form and ethyl and amyl acetates. It is reduced to mannite by ammonium sulfide. When allowed to stand, it decomposes spontaneously. Being a solid, it is not as adaptable as nitroglycerol for explosives. Curiously enough, nitrosorbitol is apparently a liquid, and of similar explosive properties. *d*-Mannose pentanitrate[1] is found as rhombic needles, m. pt. 81°-82°, and is dextrorotatory.

Nitrated Resins. The nitrated resins, especially alone, on account of their complexity and absence of chemical homogeniety have been found difficult to sufficiently stabilize for commercial purposes. They have been brought forward as absorbent material for explosive liquids.

T. Hawkins,[2] has described a fluid product for use in explosives and obtained from Australian Grass Tree gum in the following manner: The powdered gum is immersed in petroleum containing one per cent. each of acetone and oil of turpentine and nitric acid is dropped into and through the petroleum on to the gum until the latter carries the maximum of nitro-groups.

The E. Steele explosive,[3] is a product consisting of a mixture of 75 to 70 per cent. of ammonium nitrate and 25 to 10 per cent. of "nitrated or dinitrated resin or nitrated, dinitrated or trinitrated mixture of resin and cereal or starch meal. In the latter case the mixture of the nitrated, dinitrated or trinitrated resin and meal should be in such proportion that from 5 to 50 per cent. of the meal is added to the resin." The mixture may then be granulated by being exposed to the effect of atomized alcohol in the form of methylated spirits. In the manufacture of combustibles for explosives, according to the method devized by O. Carlson,[1] nitrated resin and a nitrocarbon are heated together and the product then nitrated. In the example cited, 40 parts of nitrated resin containing 3.5% N are allowed to act upon 60 parts of nitrotoluene containing 12% N at a moderately increased temperature, the product being further heated to 75°, together with 120 parts of nitric acid having a sp. gr. of 1.32, the product of reaction obtained containing 10.4% N and gives in the ratio of 20.5 to 79.5 a plastic explosive.

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[1] W. Will and F Lenze, Ber. 1898, **31**, 68; abst. Chem. News, 1898, **77**, 152; J. C. S. 1898, **74**, i, 227; J. S. C. I. 1898, **17**, 271; Bull. Soc. Chim. 1898, **20**, 390; Chem Centr. 1898, **69**, I, 441; Jahr. Chem. 1898, **51**, 1307; Wag Jahr 1898, **44**, 707; Zts ang Chem. 1898, **11**, 517.

[2] E. P. 17307, 1913; abst J. S. C. I. 1914, **33**, 569. E. Schultze (D. R P. 38363; abst. Ber. 1887, **20**, 237-R, Jahr. Chem. 1887, **40**, 2599; Wag. Jahr. 1887, **33**, 572; Chem Ind. 1887, **10**, 76, 189) has described a sporting powder composed of nitrated resin, nitrated turpentine and nitrated rosin. The powder is finally grained and waterproofed by a coating of collodion. In the W. Spore patent (U. S. P. 762446, 1904; abst. J. S. C. I. 1904, **23**, 728; Chem. Zts. 1904, **3**, 692; Mon. Sci. 1905, **63**, 15; J. A. C. S. 1905, **27R**, 60) nitrated turpentine is combined with potassium chlorate and corn pith.

[3] E. P. 11000, 1904; abst. J. S. C. I. 1904, **23**, 999. E. P. 4114, 1906; abst. C. A. 1907, **1**, 1489; J. S. C. I. 1907, **26**, 280; Zts. Schiess. Spreng. 1907, **2**, 195.

In another process[2] liquid resin is nitrated, mixed with a perchlorate, a nitrate, and optionally, ferrosilicon.

C. Bauer[3] employs nitrated colophony, resin or balsam, in order to clarify turbid, aqueous liquids. For this purpose the nitro-derivatives are finely ground with a small quantity of water or dissolved in a solvent which is miscible with water or an alkali hydroxide or carbonate solution, before being added to the solution to be clarified. When alkaline solutions are used an acid precipitant or a salt such as lead or sodium acetate is also added. When used for clarifying alimentary products, such as gelatine solutions, the nitro-derivatives must first be freed from bitter substances by dissolving in an excess of alkali hydroxide, or carbonate solution and heating to incipient saponification. As an example, a solution of 100 gm. of dextrin in 300 gm. of water is stirred in the cold with 5 cc. of a solution containing 10% of nitrated resin and 90% alcohol. The filtered and concentrated solution remaining clear for an indefinite period.

Nitrofibroin,[4] Tallöl (a liquid resin obtained as a by-product

[1] U. S. P. 1122072, 1914; abst. C A. 1915, **9**, 380; J S. C. I. 1915, **34**, 153; Mon. Sci. 1915, **82**, 51. E. P. 5707, 1910; abst. C. A. 1911, **5**, 3158; J. S. C. I. 1911, **30**, 448; Zts. Schiess Spreng. 1910, **6**, 276. In the G. v. Planitz process (U. S. P. 251145, 1881; abst. J. A. C. S 1881, **3**, 171), a base for blasting powders is formed by the combination of diluted nitric acid with resin. The H. Schoeneweg explosive (E. P. 6664, 1886; abst. Wag. Jahr. 1887, **33**, 574; J. S. C. I. 1886, **5**, 679; Chem. Ind. 1887, **10**, 189; Chem. Tech. Rep. 1887, **26**, I, 229; Mon. Sci. 1887, **29**, 574) comprizes di-, or trinitrobenzene with ammonium nitrate, which is protected against moisture by mixing it with about 5% of nitrated resin dissolved in alcohol.

[2] Nitroglycerin Aktiebolaget, Swed. P. 42470, 1917; abst. C. A. 1917, **11**, 2783. H. Hibbert (U. S. P. 994841, 1911; 12133, 67, 1213369, 1231351, 1917; E. P. 106086, 1917; abst. J. S C. I. 1917, **36**, 943; 1918, **37**, 167-A) nitrates ethylene, propylene and butylene glycol and produces explosives therefrom. Nitrocellulose is dissolved in the nitrated polyglycol.

[3] D. R. P. 292542, 1914; abst. J. S. C. I. 1916, **35**, 1123; Chem. Zentr. 1917, **88**, I, 321; Chem. Ztg. Rep. 1916, **40**, 238; Wag. Jahr. 1916, **62**, I, 380; 1917, **63**, II, 107.

[4] T. Johnson and A. Hill, J. A. C. S. 1916, **38**, 1392; abst. J. S. C. I.

in the preparation of cellulose from Swedish Pine)[1] and nitrol,[2] are of minor interest in this connection.[3]

Other Nitrated Celluloses. Various forms and sources of cellulose have been proposed from time to time for the preparation of the corresponding nitrates, with the idea in mind either of obtaining products which could successfully compete in price with nitrated cotton, or which might develop desirable technical properties of value in the explosive industries. In general these products have not found the wide technical applications predicted for them, partly due to uncertain and limited supply of raw material, but more so to the difficulty in purification, and instability and proneness to decomposition upon the long continued storage to which this class of bodies is often unavoidably subjected.

1916, **35,** 922, C. A 1916, **10,** 2223, J. C S 1916, **110,** i, 611 See also T. Johnson, A. Hill and L. O'Hara, J. A C S. 1915, **37,** 2170, abst. J. S. C. I. 1915, **34,** 1047; J. C. S. 1917, **108,** i, 1017.

[1] W. Fahrion, Zts. ang Chem 1909, **22,** 582; abst J. S C I. 1909, **28,** 431; C. A. 1909, **3,** 1697; J. C. S. 1909, **96,** i, 317, Bull Soc. Chim. 1909, **6,** 822; Chem. Zentr. 1909, **80,** I, 1477, Jahr. Chem 1909, **62,** II, 1039. E. Guignet (Compt. rend **88,** 590, J. C S. 1879, **36,** 602) has described products formed by treatment of coal with nitric acid. Oxypicric acid is one product. G. Schultz (E. P. 19565, 19565-A, 1907; Can P. 111663) has patented the nitrated products of solvent naphtha

[2] O Silberrad, E. P. 13860, 1911; abst. J. S C I. 1912, **31,** 1009; C. A. 1913, **7,** 258; Chem Ztg Rep 1913, **37,** 36. See also E. P. 13861, 1911; abst C. A. 1913, **7,** 258, J S C. I. 1912, **31,** 978; Chem. Tech. Rep. 1913, **37,** 36 E. P 19381, 1912. U. S P. 1092758, 1914. Nitrol is gelatinized by soluble nitrocellulose. Lusol is nitrated aromatic coal tar hydrocarbons (E. Raynaud, F P. 449785, 1912, J S. C. I 1913, **32,** 509)

[3] In connection with this topic see V Ansay and C. Nameche, E. P. 19993, 1907; abst. J. S. C. I. 1908, **27,** 524, Zts Schiess Spreng 1908, **3,** 256, 376 F. Gehre, E. P 342, 1908, abst. C. A 1909, **3,** 1593. O. Silberrad, E. P. 799, 1912; abst C. A. 1913, **7,** 2301; J. S. C I. 1912, **31,** 1055; Chem. Ztg Rep. 1913, **37,** 321. H. Cosway, and United Alkali Co, E. P. 8084, 1913; abst. C. A. 1914, **8,** 2603; Chem. Ztg. Rep. 1914, **38,** 252. A. Flexer, E. P. 16031, 1913; abst. J. S C. I. 1914, **33,** 347. C. Distler, E Blecher and C. Lopez, F. P. 380996, 1907; abst Mon. Sci. 1909, **71,** 10; C A. 1909, **3,** 1690 Roth, D. R. P. 39511, 1886, abst Wag. Jahr. 1887, **33,** 572; Mon. Sci. 1888, **32,** 1332. The method of the Satanite Powder Co. (E. P. 7719, 1911; abst. C. A. 1912, **6,** 2843, J. S C. I. 1911, **30,** 1186; Chem. Ztg. Rep. 1912, **36,** 531; Zts. Schiess. Spreng. 1912, **7,** 81) relates to *nitrated* mixtures of *resin* and starchy materials for use in explosives, and consists in the following process of nitration. Resin and starchy material, such as finely ground wheat, are mixed together with boiling water; the mixture is heated partially to cook the wheat, and nitric acid is added, or nitric acid is added without prior cooking; the mass is stirred, until it ceases to give off fumes of nitrous oxide, and then immediately washed with hot water, which maintains it in a pasty condition. The product thus obtained is said to consist chiefly of oxidized resin and to contain practically no nitrogen. When the mass has cooled and become dry, hard, and crystalline, it is crushed for admixture with ingredients such as a chlorate and a solvent such as wood alcohol.

As far back as 1859[1] nitrated white pine sawdust was patented as a useful waterproofing composition. Twelve years previously, C. Mosander nitrated cut straw in an unsuccessful attempt to prepare a suitable propulsive powder. E. Cotte[3] purified the straw before nitration, by digestion with soda solution and pulping, claiming for the nitrated straw an increased stability due to the presence of silicic acid in the fiber. The straw nitrocellulose of J. Lanfrey and J. Renard,[4] and patented under the name "Paleine," contained potassium nitrate, charcoal, dextrin and nitroglycerol in addition. Dolliak[5] as the result of an extensive investigation of nitrated straw, concludes it is impossible to obtain pure cellulose from straw fiber, as there always remains fat, wax, resins and proteins which, when nitrated, give rise to products

[1] J. Mackintosh and G. Rhodes, E. P. 734, 1859.

[2] Oefvers. af. K Vet. Acad. Förhandl. III, 290; Berz. Jahr. Chem. 1848, **27,** 416. P. Magnier and L. Doerflinger (E. P. 4711, 1878) have disclosed a method for the nitration of flax. See H. Vieira, F. P. 422064, 1910. E. P. 29582, 1910; abst. J. S C. I. 1911, **30,** 485 P Germain, Belg. P. 181747, 1905. J. Foltzer and F. Scheys, Belg. P. 191972, 1906

[3] E. P. 3119, 1878; abst. Wag. Jahr 1879, 418, J. C. S. 1879, **36,** 422. Prepares nitrocellulose from "various straws, such as corn, rye, barley, oats, and buckwheat " The straw is boiled with an alkaline carbonate, triturated, washed and manufactured into a sheet by a paper machine. The sheet is cut up into small pieces, which are immersed for three or four hours into nitro sulfuric acid, then washed and dried. The little pieces are then steeped in a solution of nitre and dextrin containing charcoal in suspension, drained and again dried. A "dynamite" may be prepared by mixing the crushed straw nitrocellulose with nitroglycerol. The inventor claims that the straw nitrocellulose is much more stable than guncotton, a result that he attributes to the silica contained in the straw, which he considers to play a part analogous to that which it fulfils in dynamite. Corn straw, as containing most silica, is most suitable for manufacture

[4] D. R. P. 12115, 1880; abst J. A. C. S. 1881, **3,** 76; Industriebl. 1881, 95; Chem. Tech. Rep. 1881, **20,** I, 148; Dingl. Poly. 1881, **240,** 31; Bull. Soc. Chim. 1881, **35,** 287; Chem. Ind. 1881, **4,** 55; Wag. Jahr. 1881, **27,** 331; U. S. P. 276833. F. P. 124789. Belg. P. 49853. E. P. 3119, 1878; abst. Dingl Poly. 1879, **234,** 253; Chem. Ztg. 1879, **3,** 463; Industriebl. 1879, 275; Wag. Jahr. 1879, **25,** 418; J. A. C S. 1879, **1,** 405; Ber. 1879, **12,** 1735; Chem. Tech. Rep. 1879, **18,** I, 289; Chem. Ind. 1878, **1,** 350. Aust. P. 5524. See also Mitth. Gegenst. Artill. Geniewesens, 1882, 276; abst. Dingl. Poly. 1883, **248,** 427, 509; Jahr. Chem. 1883, **36,** 1703. In F. P. 192181, 1888; Germain patented an explosive containing nitrated cocoanut fiber.

[5] Mitth. Gegenst. Artill. Geniewesens, 1882, 278; abst. Dingl. Poly. 1883, **248,** 509; 1885, **255,** 523; Berg. u. Hüttenmztg. 1882, 119; Chem. Tech. Rep. 1882, **21,** II, 176; J. S. C. I. 1885, **4,** 366; Chem. Tech. Centralanzeiger, **3,** 454; Wag. Jahr. 1883, **29,** 388. See also Wag. Jahr. 1881, **27,** 334. Chem. Tech. Rep. 1885, **24,** I, 201. Oarite, a powder proposed by G. Trench, was composed of a mixture of nitrate with various nitrated vegetable fibers and nitroglycerol. See Pochez and Piquet, F. P. 146181, 1881; abst. Mon. Sci. 1882, **24,** 734.

possessing little stability. More recently K. Nitzelnadel[1] has prepared nitrocellulose from various samples of sulfite wood pulp, bleached and unbleached, also from straw cellulose. These materials contain higher proportions of non-cellulose impurities than the cotton ordinarily employed in the nitrocellulose industry; straw cellulose also possesses the disadvantage of not being readily wetted by liquids. The nitration experiments showed that sulfite wood pulp yields products containing at least as much nitrogen as those prepared from cotton. The products from straw cellulose were generally poorer in nitrogen. The solubility in ether alcohol of the nitrocellulose prepared from these celluloses was generally over 40%; in one case only was it as low as 13%. The films obtained on evaporating the solutions were inferior to those from solutions of nitrated cotton. The stability tests, performed, according to Will's method, showed that these nitrocelluloses were sufficiently stable to satisfy official specifications; the products from straw cellulose showed the lowest stability. The ignition temperature, according to Kast's test, was in general somewhat lower than for nitrated cotton, but all the nitrocelluloses prepared from wood fiber showed temperatures of ignition well above the specified minimum limit of 180°; the products from straw cellulose tended to fall below this limit. The yields of nitrocellulose from sulfite wood pulp were lower than those obtained from cotton—straw cellulose gave the lowest yield. His conclusions are in favor of wood cellulose as a raw material in the nitrocellulose industry, but considers straw cellulose unsuitable. The disadvantages of wood cellulose, as compared with cotton are the lower yields, the lower ignition temperature of the products and the greater solubility in ether alcohol. It has been pointed out that one of the chief difficulties in preparing nitrated derivatives from wood cellulose lies in the different structure of the cells of the spring and autumn growths, and it is possible that woods grown in the tropical regions would afford more uniform results under chemical treatments.

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[1] Dissertation, Dresden; Zts. Schiess. Spreng. 1912, **7**, 257, 301, 339, 384, 409; abst. C. A. 1913, **7**, 257, 892, 1611; J. S. C. I. 1912, **31**, 954; Wochbl. Papierfabr. 1912, **43**, 3488; Chem. Zentr. 1912, **83**, II, 2157; Wag. Jahr. 1912, **58**, I, 438; Mon. Sci. 1913, **78**, 630. Claim is made for the utilization of cellulose obtained from gorse for preparing nitrocellulose for various purposes, in the processes of G. Horteloup (F. P. 371136; abst. Mon. Sci. 1903, **59**, 195. F. P. 331176, 1903; 347353, 1904; abst. Chem. Ztg. 1905, **4**, 89; J. Soc. Dyers Col. 1905, **21**, 86. E. P. 26150, 1903; abst. J. S. C. I. 1904, **23**, 500. E. P. 21505, 1905; abst. J. S. C. I. 1906, **25**, 441) and M. Wertz (E. P. 12422, 1910; abst. J. S. C. I. 1911, **30**, 798; Chem. Ztg. Rep. 1911, **35**, 520; 1912, **36**, 332; Mon. Sci. 1916, **83**, 47; J. Soc. Dyers Col. 1911, **27**, 214). According to Sci. Amer. 1917, **116**, 575, the beet has been used as a substitute for cotton in the manufacture of nitrocellulose.

According to a patent issued to Spooner and the Pyroxylin Manufacturing Co.,[1] a nitrocellulose for use as an explosive for preparing collodion, or for making dental plates, is made by nitrating the fibers of the esculapius weed, the fibers being treated in the usual manner. N. Ceipek[2] claims a mixture of 80 to 90 parts of ammonium nitrate and 20 to 10 parts of nitrated turmeric as a superior safe explosive requiring 2 grams for explosion. In an early United States patent[3] fibers of Asclepias syriaca, commonly called "silk weed" or "milk weed" are described as especially suitable for guncotton manufacture.

F. Greening[4] prepares a base by treating esparto grass with a mixture of fuming nitric and sulfuric acids, washing, neutralizing and finally drying, which is then dissolved in amyl acetate and used as a liquid coating or varnish. Esparto grass[1] ramie,[2] rhea, china grass,[3] horny materials,[4] sisal,[5] cottonseed hulls[6] are among the materials which have engaged the attention of investigators from time to time as possible substitutes for cotton cellulose for nitration purposes.

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[1] D. Bickford, Spooner and the Pyroxylin Manufacturing Co, E. P. 1170, 1873; abst. Ber. 1875, **8,** 171; Wag Jahr 1875, **21,** 532; Chem. News, 1874, **29,** 74; Chem. Tech. Rep. 1875, **14,** I, 217.

[2] E. P. 7838, 1907; abst. C. A. 1908, **2,** 1069; J. S. C. I. 1907, **26,** 1296; Zts. Schiess Spreng. 1908, **3,** 96. E. P. 9742, 9743, 1911; abst. C. A. 1913, **7,** 703; J. S. C. I. 1911, **30,** 926; Zts. Schiess. Spreng. 1912, **7,** 33. E P. 13549, 1911; abst. C. A. 1912, **6,** 3525, J. S. C. I. 1911, **30,** 1232. F. P. 381484; abst. C. A. 1909, **3,** 1690. U. S. P. 1033537; abst. C. A. 1912, **6,** 2687; Mon. Sci. 1913, **79,** 13; Zts. Schiess Spreng. 1913, **8,** 16. Hung. Anm. C-1908, C-1909, 1910. F. P. 428748, 1911, and addn. 14417 thereto The original material (J. S. C. I. 1911, **30,** 926) was called "titanite," and manufactured at Corey, Pa., by W. A. Clark Explosive Co.

Turmeric, preferably in powder and previously extracted with hot water to remove the coloring substances is dried and treated with a nitrating mixture composed of 33% of nitric acid, 45.5% sulfuric acid, and 21.5% of water, the mixture being used preferably in the proportions of 10 parts by weight to one part by weight of turmeric. The finely ground, and sifted material is added in successive small quantities into the nitrating acids with constant stirring until a uniform mixture results. When the entire quantity of the treated material has been introduced, an equal quantity of cold water is then added whereupon the stirring is interrupted and the whole mixture left to rest until a powder of light yellow color has been precipitated. After the reaction has subsided the acid is drained off and the nitrated body washed and dried. In this manner, according to the claims of the patentee, a product is obtained which is insensitive to blows or shocks. See also P. Caminada, E. P. 6761, 1914.

In the process of A. Bang and C. Clolus (E. P. 1811, 1881) cotton, flax, hemp, jute or other vegetable fabrics are treated with a mixture of nitric and sulfuric acids. The acid bath is of such strength that the materials are not rendered explosive, the cellulose being only partly nitrated. The materials so treated can be dyed like silk, wool, etc., with aniline dyes, indigo, or litmus, without the use of mordants.

[3] J. McLean, U. S. P. 47316, 1865.

[4] E. P. 5344, 1899. This process is anticipated by that of S. Mackie, C. Faure and G. Trench, E. P. 2742, 1876; abst. Ber. 1876, **9,** 650; Dingl.

R. Bernstein[7] employs the solid fruits, nuts, or nut shells of

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Poly. 1876, **221**, 94; Deut. Industrieztg. 1876, 228; Wag. Jahr. 1876, **22**, 479, Bayer. Ind u. Gewerbebl. 1876, 141. For treatment of esparto according to the process of L. Trigos, see F. P. 480606, 1916; abst. J. S. C. I. 1917, **36**, 131.

[1] W. Henley and D. Spill, E. P. 1017, 1870; abst. J. S. C. I. 1893, **12**, 709; Mon. Sci. 1913, **78**, 392. He had difficulty in removing silica from the esparto. See Jour. Chem. Soc. 1894, **89**, 137. C. Hengst, E. P. 18002, 1898; abst. Mon. Sci. 1900, **56**, 131; J. S. C. I. 1899, **18**, 787.

[2] E. Nowicki, F. P. 402197, 1909; abst. Rev. Chim. Ind. 1909, **20**, 325; J. S. C. I. 1909, **28**, 1274. Belg. P. 215662, 1909.

[3] L. Deitz and B. Wayne, U. S. P. 133969, 1872. At the time of the issuance of this patent, both Deitz and Wayne were associated with Hyatt in the billiard ball business. At that time it was found that billiard balls made substantially wholly of nitrocellulose would soften by impact and in order to produce a hard pyroxylin they were led to undertake these experiments with ramie, rhea and China grass. They claim that pyroxylin made from ramie will always be of uniform strength and solubility, and that in making collodion from this pyroxylin a much smaller quantity of solvent is required than for pyroxylin made from cotton. Subsequent experiments, however, have not corroborated their contention.

[4] L. Notelle and L. Leroux, F. P. 347702, 1904; abst. J. S. C. I. 1905, **24**, 450; C. A. 1907, **1**, 663; Mon. Sci. 1906, **65**, 143. They submitted horn to the action of nitric acid to obtain a product analogous to nitrocellulose, in which the horn was washed with dilute alkaline water, and left for one or two months in a bath comprising water 95.5, nitric acid 2, sulfuric acid 0.5, and zinc chloride 2. After thoroughly washing and soaking in a solution of water 83, tannin 2, alcohol 20 and dextrin 50 for eight days, the product is drained and then dried.

[5] R. Hollins and T. Taylor, E. P. 23192, 1908; abst. J. S. C. I. 1909, **28**, 1270; C. A. 1910, **4**, 1544; J. Soc. Dyers Col. 1910, **26**, 13.

[6] C. Hengst, E. P. 13656, 1888; abst. J. S. C. I. 1889, **8**, 478; E. P. 20978, 1890; abst. J. S. C. I. 1890, **9**, 325.

[7] E. P. 5055, 12778, 1885; abst. J. S. C. I. 1886, **5**, 516; 1887, **6**, 225. U. S. 363197, 1887; abst. J. A. C. S. 1887, **9**, 125. F. P. 172309, 1885; abst. Mon. Sci. 1886, **28**, 843. D. R. P. 36061, 1885; abst. Jahr. Chem. 1886, **39**, 2081; Ber. 1886, **19**, 636; Wag. Jahr. 1886, **32**, 319. Belg. P. 70865, 1885. It. P. 19109, 1885. Span. P. 8178, 1886.

E. Harris (E. P. 13691, 1912, abst. C. A. 1913, **7**, 4050; J. S. C. I. 1913, **32**, 748; Chem. Ztg. Rep. 1913, **37**, 592) proposes to utilize the whole of the ivory nut especially that which has hitherto been discarded as waste material, in which he grinds the vegetable ivory to a powder and this in turn is formed into a plastic condition by the addition of viscose with a sufficient amount of water; the plastic mass being pressed and molded into convenient shapes for the formation of the articles desired. The articles are finally dried by exposure to the atmosphere at normal temperature, being finally heated to about 100°.

The average composition of vegetable ivory is shown by the following trees of the palm species, particularly the product of "Phytelephas macrocarpa," usually known as vegetable ivory and of several species of "Mauritia," or the sawings or turnings of these, which are pulverized, boiled in alkalis, washed with water, and then nitrated in the usual manner. The powder thus obtained may be used for the manufacture of celluloid. The use of nitrated vegetable ivory as a smokeless powder constituent was patented in 1891,[1] and for dynamite in 1915.[2]

A. Hart[3] has described nitrocelluloses prepared from fibers analysis.

Moisture (loss at 75° after 18 hours)	6 7%-7 5%
Ether extract	1 1%-2%
Extraction with 100 volumes of water	6% -7%
Extraction of hydrochloric acid (1 to 10) .	2% - 2 5%
Hydrolysis with HCl (2 cc HCl to 150 cc. water, boiled 20 minutes)	12% -15%
Residue . . .	65% -70%

According to O Guttmann (Dingl. Poly 1888, **268,** 519, abst. J. S. C I 1888, **7,** 588, Rev. Chim Ind 1890, **1,** 165; Rev Sci 1889, **44,** 220, Tech Chem Jahr. 1889, **11,** 183; Chem Ind 1888, **11,** 556; Chem Tech. Rep 1888, **27,** II, 223) a vegetable ivory explosive known as Meganite consists of

	Nitro-glycerol	Nitrocellulose from Wood		Added Powder
		Wood	Vegetable Ivory	
Meganite No 1	60	10	10	20
Meganite No 2 . .	38	6	6	50
Meganite No 3	7	9	9	75

The added powder was for No 1, $NaNO_3$, for Nos 2 and 3, $NaNO_3$ 75%; Na_2CO_3 1%, wood meal or rye meal 24%.

[1] Dynamit Actienges. Nobel, F. P 172309, 1885, abst. Mon Sci 1886, **28,** 843. F P. 186801, 1887, abst Mon Sci 1888, **32,** 883. E. P. 6129, 1891; abst J S. C I. 1892, **11,** 267, 456

[2] C. Stine, U. S. P. 1143330, 1915, abst C. A. 1915, **9,** 2313, J S C. I. 1915, **34,** 852, Chem Ztg Rep. 1916, **40,** 242 U. S. P. 1313650; abst C. A. 1919, **13,** 2763. E P 142303, 1919, abst. J S. C I 1920, **39,** 469-A. Can. P. 198328, 1920, nitrates hemicellulose such as is obtained from ivory nut, and uses as a detonator charge together with TNT, picric acid, lead azide and mercury fulminate. Nitrated hemicellulose is said to be especially suitable for detonating dynamite For "nitro-semicellulose," see Vereinigte Köln-Rottweiler Pulverfabriken, E. P. 5126, 1904; abst J S. C I. 1904, **23,** 560; Chem. Ztg 1905, **29,** 751; E. P 3937, 1914

[3] E. P. 18606, 18607, 1910; abst. J. S. C. I. 1911, **30,** 1446; C. A. 1912, **6,** 1531; Chem. Ztg. Rep 1912, **36,** 13; J. Soc Dyers Col. 1912, **28,** 44. Belg. P. 237894, 1911. In A Hart, E. P. 18607, 1910 (abst. J. S. C. I. 1911, **30,** 1448; C. A. 1912, **6,** 1531; F. P. 433012, 433013, abst. J. S. C. I. 1912, **31,** 123, 1133; Mon. Sci. 1913, **78,** 24) fabrics, yarns, paper, leather and cords are waterproofed by treatment with a composition consisting of non-explosive nitrocellulose described above, dissolved in ether and methylated spirit, mixed with the oil described in E. P. 11340, 1909 (abst. C. A. 1909, **3,** 2385, abst. 1911, **5,** 1202) and diluted with methylated spirit. For fireproofing, sodium tungstate is mixed with a little of the oil and added to the mixture, and for coloring, a pigment is powdered, boiled in water, separated, dried, mixed with a little methylated spirit and added to the composition.

such as those of Poseidonia Australio (Calotropis gigantea) and hemp such as "Sansevieria" by freeing them from gums by soaking them in water or boiling with alkali, steeping the gum-free fiber in dilute sulfuric acid, washing, drying, garnetting, and nitrating, and after pressing out excess of acid, again washing and finally drying.

A. Carneiro[1] has conducted extensive investigations of fibers and flower stalk of Agave Americana and Agave Prostrata, and collected a great number of agave fiber analyses which are published by K. Braun, in "Pflanzer." It was found that the cellulose proportion of the agave varies between 64.6% and 82.4% and the ash from 2.64-2.80%. The author has also made as pure cellulose as possible from the flower stalk and nitrated these; he gives the details of nitration and the constants of products obtained in table form The fiber was scoured with sodium carbonate, bleached and nitrated in a mixture of 1 part nitric to 2 parts sulfuric acids, the nitrogen content of the resulting product varying within the limits 11.5-12.1%.

The process of J. Wilson[2] relates to the preparation of fibrous material from the plant Bauhinia Vahlii, the dried stems of which are rubbed between roughened rollers which have a rotary and longitudinal reciprocating motion to disintegrate the fibers and separate the bark. The fibers are washed and treated with an oxidizing agent and after drying are then said to be applicable for the preparation of nitrocelluloses.

H. Kolf[3] proposes to nitrate malt grains, malt meal and waste products from ash, moss, beets, bread fruit and althea root, while E. Kopp[4] apparently was serious when he proposed to nitrate sheep's wool, as was Pochez and Piquet when they described

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[1] Zts Schiess Spreng. 1909, **4,** 103, J S C. I. 1909, **28,** 384; Jahr. Chem 1909, **62,** II, 389, Chem Zentr 1909, **80,** I, 1412, C. A. 1909, **3,** 1928.

[2] E P 12532, 1886 D R P 62159, 1891.

[3] D R P. 56786; abst Wag. Jahr 1891, **37,** 434; Zts. ang. Chem. 1891, **4,** 306, Jahr. Chem. 1891, **44,** 2667, Ber. 1891, **24,** 1005-R, Chem. Ztg. 1891, **15,** 964; Chem Tech. Rep. 1891, **30,** I, 219; Bull. Soc. Chim. 1892, **40,** 37; Meyer Jahr Chem. 1891, **1,** 330. D. R. P. 62159; abst. Zts. ang. Chem 1892, **5,** 435; Chem Ztg 1892, **16,** 962; Chem. Tech. Rep. 1892, **31,** II, 165, Chem. Ind. 1892, **15,** 377, Wag. Jahr. 1892, **38,** 377; Ber. 1892, **25,** 711-R, Industriebl. 1892, 247; Tech. Chem. Jahr. 1892-3, **15,** 174, Meyer Jahr. Chem 1892, **2,** 363.

[4] Mon. Sci 1874, **16,** 499, abst Wag. Jahr. 1874, 423. Gintl (Ber. ueber die Zuendwarren 1874, 31) alleges the wool is nitrated. V. de Cornelian (E. P. 852, 1862) has patented a method for preparing guncotton from the waste silk fibers remaining in cocoons.

methods for the nitration of animal refuse and the waste silk fibers remaining in cocoons after the long fibers have been removed.[1] The method of J. Cochran,[2] for the utilization of the fuzz from cotton seed hulls for formation into cellulose useful for the manufacture of nitrated products, has received serious consideration. Cochran obtains the fuzz from cotton seed hull by removing all of the staple fiber and lint from the seed and then mechanically reclaiming the fuzz in a pure and unchanged condition. The fuzz is subsequently bleached and nitrated in the usual manner. Difficulty has been found in the nitration of cotton seed fuzz in obtaining first, acceptable yields, and second, a product of desired stability.

In the utilization of flax, hemp, jute and ramie for the preparation of cellulose suitable for the manufacture of collodion, celluloid and guncotton,[3] A. Bouret and F. Verbiese soak the fiber first in a dilute solution of sodium carbonate, then in bicarbonate of soda, the material meanwhile being agitated by a rotary stirrer operated by mechanical means from the outside of the vessel. The process is completed by subsequent bleaching and drying.

W. Eales[4] has described a fuse which is prepared from nitrated flax or hemp fiber saturated with potassium nitrate, chlorates, chromates or picrates.

The process of the Gocher Oelmühle[5] is similar. A. Vournasos[6] nitrates the tow obtained from the stems of Hibiscus

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[1] F. P. 146181, 1881; abst. Mon Sci. 1882, **24,** 734.

[2] E. P. 12920, 1906; abst. C. A. 1907, **1,** 2512; J. S. C. I. 1907, **26,** 775. G. Audemars (E. P. 283, 1855) proposed the fibers and bark of the mulberry tree, especially for artificial silk formation. Reeves and Muschamp (E. P. 3293, 1866) proposed rags and vegetable fibers treated with soda, and then pulped and formed into sheets. Cotton lint from cotton seed hulls was proposed by G. Mowbray (E. P. 20978, 1891) and Arkins (E. P. 7058, 1903) and machinery for preparing this material was invented by Minck & Bremer Baumwolle Akt Ges. (E. P. 12718, 1906) and Cochran (E. P. 12920, 1906). Pipitz (E. P. 18935, 1895) advocated alder wood shavings

[3] E. P. 24768, 1898; abst J S C. I. 1900, **19,** 42. E. P. 27303, 1910, J. René, described the treatment of kapok for nitrating, which is used in ethereal solution. W. Thompson, W. Severn and G. Twycross (U. S. P. 1302455, 1919; abst. J. S. C. I. 1919, **38,** 480-A) claims the use of nitrated baobab wood or fiber for nitrocellulose.

[4] D. R. P. 1853, 1877; abst. Wag. Jahr. 1878, **24,** 466; Chem. Ind. 1878, **1,** 275. For nitration of fibers of Ulex Europens, see G. Hourteloup, F. P. 327136, 1902; 331176, 1903; 347533, 1904; abst. Mon. Sci. 1903, **59,** 195.

[5] F. P. 366125; abst. J. S. C. I. 1906, **25,** 1001; C. A. 1907, **1,** 2432; Mon. Sci. 1907, **67,** 102. See also E. P. 3211, 1906; abst. J. S. C. I. 1906, **25,** 865; C. A. 1907, **1,** 640. Belg. P. 190009, 190154, 1906.

[6] E. P. 9547, 1914; abst. C. A. 1917, **11,** 539; J. S. C. I. 1917, **36,** 164.

Cannabinus and its various species of the natural order Malvacae, the tow being obtained by rendering the green stems, preferably by steeping them in running water, then by scutching and combing and finally exposing the newly combed tow to sunlight.[1] A fine and white nitrocellulose is claimed to result by subjecting this tow to a preliminary bleaching with chlorine and nitrating in the usual manner.

J. Bourbon and P. Cassier,[2] P. Joliot[3] and A. Bloch[4] describe artificial cotton claimed as suitable for the preparation of cellulose nitrates of low and high nitration made from the cellulose of the fir tree freed from bark and knots.[5] The Australian Grass Tree Gum;[6] leaves of plant and trees belonging to the Australian Eucalypti and the Australian Melaleuca,[7] by treatment of the brittle vegetable fibers of kapok[8] and of certain Musinees and Spagnees[9] together with the pith[10] and stems of maize[11] are examples of the versatility of vegetable products which apparently have been seriously considered as a substitute for cotton in the formation of cellulose nitrate products, and especially plastics.

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[1] E. P. 17348, 1914; abst. C. A. 1917, **11**, 539; J. S. C. I. 1917, **36**, 131. 30 parts by weight of the fibers are immersed in a mixture of 250 parts of HNO_3 (sp. gr. 1.38) and 500 parts H_2SO_4 (sp. gr. 1.82) for 24 hours at 15°. Either the crude or the bleached fiber may be used. The product, called "cellulose vournasos, is a pure, white nitrocellulose, and of unusually high stability.

[2] F. P. 429679, 1911; abst. J. Soc. Dyers Col 1911, **27**, 224.

[3] F. P. 469446, 1913; abst. Mon. Sci. 1916, **83**, 65.

[4] F. P. 447068, 1911.

[5] J. Frank. Inst. 1904, **158**, 467; Jour. Soc. Dyers Col. 1905, **21**, 46.

[6] Powerite Explosive Co., E. P. 19267, 1914, abst J. S. C. I. 1915, **34**, 890; Mon. Sci. 1917, **84**, 80. See also E P. 17307, 1913; abst. J. S. C. I. 1914, **33**, 569. The preferred composition of the explosive is: nitroglycerol, 40; nitrocellulose and nitrated Australian grass tree gum, 20 each; calcium picrate, 2; potassium nitrate, 10; wood meal, 3; and castor oil, 1 part.

[7] T. Kelly, G. Bell and R. Kirk, E. P. 8680, 1899; abst. Arms and Explos. 1899, **7**, 195; Chem. Ztg. 1900, **24**, 739; Mon. Sci. 1900, **56**, 21. H. Nishida (Kogyo-Kioagaku Zasshi, 1915, **18**, 18; J. Ind. Eng. Chem. 1916, **8**, 1096; C. A. 1916, **10**, 966; 1917, **11**, 209) has given the analytical constants and yields of cellulose nitrate prepared from unsized tissue papers made from mitsumata and from mulberry fibers. Nitration products of the former are of good quality, but yields are lower than for cotton. Results from mulberry are said to be fairly good.

[8] E. Stark, U. S. P. 1006142, 1911; abst. C. A. 1912, **6**, 161.

[9] R. Leuschel, D. R. P. 105877; abst. Wag. Jahr. 1899, **45**, I, 422. E. P. 8409, 1899; Zts. ang. Chem. 1899, **12**, 1064; Chem. Centr. 1900, **69**, I, 495; Jahr. Chem. 1899, **52**, 1306; Chem. Ztg. 1899, **23**, 1062; Mon. Sci. 1900, **56**, 131. J. S. C. I. 1899, **18**, 858.

[10] H. Wiley, U. S. P. 673070, 1901; abst. J. A. C. S. 1902, **24**, 65.

[11] F. Stewart, U. S. P. 1017023, 1912; abst. J. S. C. I. 1912, **31**, 279; C. A. 1912, **6**, 930.

E. Omar[1] in his series of recent patents, has described nitrocompounds prepared by nitrating lignone sulfonic acid or its salts obtained from waste sulfite cellulose lye, the process being effected by concentrating the lye free from ligneous sulfonates and nitrating with nitric or mixed acid. The nitro-compounds are precipitated or are separated by the addition of sulfuric acid, being subsequently neutralized by washing.

The explosive Titan has been described as vegetable fiber rendered explosive by treatment with nitrating acids.[2]

C. Müller[3] has described the preparation of artificial silk, photographic films and similar cellulose products obtained from a cellulose solution formed by either dissolving the best sheet fibers obtained from hop runners in copper oxide ammonia or in a mixture of nitric and sulfuric acids.

A. Hart[4] prepares nitrocellulose from the fibers of Poseidonia australis and sansenviera, by freeing them from gums by soaking in water or boiling with alkali, steeping the gum-freed fiber in dilute sulfuric acid, dry, garnetting, and nitrating. Fibers from the plant "Hedychium coronarium" have also been suggested.[5]

None of the products above described have entered the com-

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[1] E. P. 103649, 103651, 103652, 103653, 103654, 103655, 1917, abst C. A. 1917, **11,** 1749, 1750; J S. C I. 1918, **37,** 121-A, 146-A, 641-A; Chem. Ind. 1918, **41,** 140, Mon. Sci 1918, **85,** 75

[2] C. Dittmar, U. S. P. 145403, 1873

[3] E. P. 5659, 1912; abst. C. A 1913, **7,** 2856, J S C I. 1913, **32,** 133; J. Soc. Dyers Color. 1912, **28,** 164; 1913, **29,** 91. D. R. P 256351, 1911; abst. C. A 1913, **7,** 1892; Kunst. 1913, **3,** 79, 95; Zts ang. Chem 1913, **26,** I, 175; Chem. Zentr. 1913, **84,** I, 867, Chem. Ztg. Rep. 1913, **37,** 116

[4] E. P. 18606, 1910; abst. C. A. 1912, **6,** 1531; J. S. C. I 1911, **30,** 1446; Chem. Ztg Rep. 1912, **36,** 13. See also F. P. 327136, 1902; 331176, 1903; abst. Mon. Sci. 1903, **59,** 195 F P 433012, 433013, 1911, abst. J S C. I. 1911, **31,** 124. E P 18607, 1910; abst J. S. C. I. 1911, **30,** 1448. Ital P. 125163.

[5] Faria & Co, E. P. 29582, 1910; abst J. S. C. I. 1911, **30,** 485 H. Davoine, F. P. 470606, 1914; abst J. S. C. I. 1915, **34,** 172; Mon. Sci 1916, **83,** 65.

According to L. Vignon and P. Sisley (Bull. Soc. Chim. 1891, (3), **6,** 898; J. C. S. 1892, **62,** 1111) when silk is immersed in ordinary nitric acid (sp. gr. 1.133) at 45° for one minute, and is subsequently washed in water, it is colored intensely yellow, and the color is unaffected by exposure to air and light, while it is deepened by the action of dilute alkali solutions. Nitric acid free from nitrous compounds does not cause this coloration, which is found to vary in intensity directly with the amount of nitrous compounds present, and with the temperature and specific gravity of the acid used. The deepening of color by alkaline solutions is independent of their causticity, mercial field as serious competitors for the preparation of nitrocellulose.

R. Robrecht[1] treats Sönn hemp for 12 hours at 25° or under with a mixture of 3 volumes of concentrated H_2SO_4 and one volume of concentrated HNO_3; changing the fibrous nitrate to an impalpable powder by solution in sulfuric acid and precipitating with water; finally drying and gelatinizing with acetone.

Recently B. Smart,[2] and with P. Pecover[3] have made a critical study of the possible utilization of the fibers of marine fiber (*Poseidonia australis*) for the manufacture of nitrocellulose. This aquatic plant is obtained by dredging to a depth of 7 feet from certain flats on the shore of Spencer's Gulf, Australia. When nitrated in the usual manner, a yield of 72% of a 12.3% N product was obtained, which gave quite satisfactory heat tests

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while the silk increases in weight and takes up a certain amount of the base.

Silk treated with a mixture of hydrochloric acid and sodium nitrate is colored pale yellow, the color is rapidly browned on exposure to air and light, or by the action of boiling water or alcohol, while cold alkaline solutions turn it reddish brown. Silk which has been subjected to the action of nitrous acid, or of nitric oxide, in an atmosphere of carbonic anhydride, and subsequently well washed, is colorless, but is colored a stable yellow by nitric acid. Nitric peroxide colors silk yellow at once. Silk heated with nitrous acid, and then oxidized with potassium permanganate and hydrochloric acid, is colored exactly as by nitric acid (impure), from which it seems that the yellow coloration is dependent on the action of nitrous compounds, and subsequently of an oxidizing agent.

The yellow color is discharged by acidified stannous and chromous chloride solutions. Analyses of the nitrated silk show that about 2% of nitrogen is fixed in the reaction, probably, primarily, as the nitroso group, which the further action of the nitric acid converts into the nitro group, a carboxyl group being displaced. The properties of the product somewhat resemble Millon's xanthoproteic acid, but this contains more carbon and less nitrogen, and results from a more intense action. Sulfuric acid dissolves ordinary silk gradually to a slightly colored solution, whereas nitrated silk is converted into a pale yellow viscid mass. Aqueous potash dissolves ordinary silk in the cold, and nitrated silk on heating; neither solution is precipitated by dilution with water, and both evolve ammonia when heated. Both varieties of silk are dissolved by hydrochloric acid and by zinc chloride solution.

Ammoniacal vapors are evolved on distillation of each variety, and a carbonaceous residue is left. For nitration of horn, see F. P. 347702, 1904; abst. C. A. 1907, **1**, 643; Mon. Sci. 1906, **65**, 148. For the conversion of fibroin into nitrofibroin (fibroin-xanthoproteic acid), see T. Johnston, A. Hill and L. O'Hara, J. A. C. S. 1915, **37**, 2170; abst. J. S. C. I. 1915, **34**, 1047.

[1] E. P. 8604, 1906; abst. C. A. 1907, **1**, 800; J. S. C. I. 1906, **25**, 1068; Zts. Schiess. Spreng. 1907, **2**, 12. F. P. 364973, 1906; abst. J. S. C. I. 1906, **25**, 953; C. A. 1907, **1**, 2959; Mon. Sci. 1907, **67**, 122. Dan. P. 8910, 1906.

[2] Chem. Eng. Min. Review, 1918, **10**, 380; abst. C. A. 1919, **13**, 262.

[3] J. S. C. I. 1918, **37**, 300-T; abst. C. A. 1919, **13**, 262; Chem. Zentr. 1919, **90**, IV, 163.

and showed promise as a source for guncotton manufacture.

O. Fürth and E. Scholl[1] have reported upon the nitration products of chitin (see page 325), they having obtained by the action of fuming nitric acid, two nitro products, one being insoluble in the ordinary solvents, whereas the other is soluble in alcohol, acetone, ethyl acetate, and acetic acid, but insoluble in ether, petroleum ether, benzene and chloroform. In this respect there is a strong analogy to the nitrocelluloses; also exploding with the evolution of fire, lose their nitrogen in a nitrometer or by treatment with ferrous sulfate, and hydrolyze with either acids or alkalis.

Pyroxylins of Low Nitrogen Content. Much experimental work has been recorded in endeavors to reduce both the cost and inflammability of cellulose nitrate products by introducing the minimum amount of nitric acid into the cellulose molecule which will at the same time produce esters of physical properties commercially valuable. Knecht[2] has described unstable cellulose nitrates prepared by treating cellulose with nitric acid of varying strengths (sp. gr. 1.1–1.415), the neutralized products containing 3.0%–35.8% nitric acid in combination, equivalent to 0.7%–8.0% nitrogen.[3] A. Voigt[4] obtained gelatinous products by combining both the nitrating and pulverizing processes in one. He immersed cotton in 97 parts conc. sulfuric acid and 3 parts nitric acid at 2°–3°[5] and obtained after neutralization and drying a very fine powder of high stability, which the patentee considers very advantageous for the manufacture of shooting and blasting powders and of lacquers. No statements of solubility, however, are given.

In 1908 B. Herstein[6] patented methods of formation of structureless nitro derivatives of cellulose, insoluble in alcohol, ether, amyl acetate and acetone; containing less than 4.5% nitrogen, and which are transformed into a transparent or translucent mass by the addition of caustic soda. The cellulose in the form of thin paper or cotton is immersed in an acid mixture consisting of about 63% by weight of absolute sulfuric acid, about 10% nitric acid, and the remaining 27% partly water and partly other inert material. This mixture may conveniently be obtained by adding to 85 parts by volume of sulfuric acid 1.84 sp. gr., 15 parts nitric acid by volume of 1.42 sp. gr. As soon as the cellulose is immersed, visible reaction takes place, the entire mass of cellulose loses its structural form, and is converted into a gelatinous transparent magma. It is essential that the acids be cooled to a low temperature (below 20°), in order that the cellulose may not dissolve in the acid mixture, and to insure that it becomes gelatinized merely. After a few minutes' immersion the excess of acid is poured off and the residue repeatedly washed with large quantities of cold water, pressed, and dried at a low temperature. The actual percentage of nitrogen varies materially with the method of manufacture, but is seldom over 4%. The most characteristic reaction of the product is its deportment when brought in contact with caustic alkali solutions, in which it quickly gelatinizes, forming a plastic, transparent mass, readily moldable, and which may be diluted with water and forced through fine orifices. It is readily hardened or coagulated by treatment with weak acids, and combines with phenol, resorcinol, or pyrogallol, the latter property differentiating it from true cellulose nitrates. J. Crane and C. Joyce[1] have elaborated upon this process and investigated the formula of the derivatives produced and the mechanics of the several reactions. In their preferred method, paper cut in small pieces is immersed in a mixture of 65.5% sulfuric acid, 9% nitric acid, and 25.5% water, the

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[1] Beitr. Z. Chem. Physiol. u. Path. 1907, **10**, 188; abst. Chem. Zentr. 1907, **78**, II, 910; Biochem. Zentr. 1907, **6**, 642; C. A. 1907, **1**, 3020; J. C. S. 1907, **92**, i, 994.

[2] Ber. 1904, **37**, 549; abst. J. S. C. I. 1904, **23**, 335.

[3] None were entirely gelatinized products, and no statement of their solubilities is given.

[4] U. S. P. 855869, 860776, 1907; E. P. 5126, 1904; abst. J. S. C. I. 1907, **26**, 780.

[5] The scoured and cleaned cotton cellulose is immersed in conc. sulfuric acid at 2–3°, in the ratio of 5 times by weight of acid to cellulose. The fibers rapidly disintegrate with a rise in temperature. After the structure has been destroyed, about 2 k. conc. nitric acid is added, the temperature of the mixture being kept down by artificial means. After two to three hours the mass congeals into a solid cake which is washed out in large quantities of water and dried. Thus prepared the product is a fine powder.

[6] U. S. P. 879871, 1908; abst. J. S. C. I. 1908, **27**, 353. D. R. P.

214193, 1908; abst. Wag. Jahr. 1909, **42**, II, 555; Zts. ang. Chem. 1910, **23**, 384; Chem. Zentr. 1909, II, 1398; Chem. Tech. Rep. 1909, **33**, 627; Chem. Ind. 1909, **32**, 705; C. A. 1910, **4**, 500; Jahr. Chem. 1909, 390.

[1] J. S. C. I. 1910, **29**, 540 with bibliography of 18 citations; abst. J. C. S. 1910, **98**, i, 364; J. Soc. Dyers and Color. 1910, **26**, 218; C. A. 1910, **4**, 2206; Jahr. Chem. 1910, 423. See also Eighth Inter. Cong. Applied Chem. 1912, **25**, 587; abst. Kunst. 1913, **3**, 313. Hake and Bell, J. S. C. I. 1909, **28**, 457; J. C. S. 1909, **96**, i, 457. Compare C. Hake and P. Louis, J. S. C. I. 1905, **24**, 374; abst. J. C. S. 1905, **88**, i, 512. C. Cross, E. Bevan and Jenks, Ber. 1901, **34**, 2496; abst. J. C. S. 1901, **80**, i, 672.

ratio of acid to cellulose being at least 100 to 1. The temperature of the bath is kept at 5°–10° and 6–12 minutes the preferred period of immersion.[1] After nitration the mass is immediately plunged into cold water, and the lumps or "curds" obtained rapidly washed until neutral. Combustions of the product previously dried in vacuo at 50° to constant weight gave results corresponding to a mono-nitrate on a C_{12} molecule for cellulose, the yield being about 110%, against 119% theoretical for a mono-nitrate, thus showing considerable loss by solution in the acid.[2] It was found to dissolve in strong acids, strong bases (including trimethylamine), pyrogallol, Schweizer's reagent, and zinc chloride solutions. The anhydrous product was insoluble in acetic anhydride, but upon the addition of a small amount of water, acetation ensued and a product readily soluble in acetone but incompletely in chloroform resulted.[3] It is evident that these lower cellulose nitrates have valuable possibilities.

Recovery of Nitrocellulose. In the method of J. Delpech[4] for the recovery of pure colloidal pyroxylins from their solutions for explosives, the collodion is treated with a liquid (e. g., water or chloroform) which coagulates the pyroxylins, and enables them to be rapidly and economically separated.

In the method of the Vereinigte Cöln-Rottweiler Pulverfabriken for the precipitation of nitrocellulose from organic solvents,[5] solutions of nitrocellulose in acetone or other solvent are diluted with water, after which an electrolyte, e. g., alum, is added, and the solutions are then intimately mixed with organic compounds which are insoluble in water and have a slight gelatinizing action on nitrocellulose. Suitable compounds are toluol, xylol, aniline, methylaniline, dimethylaniline, carbon tetrachloride, pine needle oil, chloroform, and carbon bisulfide. The nitrocellulose is precipitated as a dense mass which can be readily mixed with the organic compounds, the resultant product being employed for the manufacture of varnishes or lacquers. The boiling solvent is diluted with water, an electrolyte is then added, and heating is continued until the nitrocellulose settles out in the form of grains, which can easily be separated from the supernatant liquid. The yield may exceed 90% of the dissolved nitrocellulose. The exploding point of the precipitated material is 180° or above.

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[1] Decrease in temperature or time lowered the gelatinizing action on the cellulose. Increase in temperature gave buttery products, partially miscible with water and indicating a breakdown of the cellulose aggregate.

[2] The sulfur was determined by the method of Hake and Lewis (J. S. C. I. 1905, **24**, 376), and nitrogen by the Dumas method in preference to the Lunge nitrometer, the latter giving incorrect and lower results, a proof that the nitrogen is present in the form of nitrate-nitrogen.

[3] It contained 2.32% N, indicating it was a completely acetylated derivative of the formula $C_{22}H_{31}O_{18}N$, similar to the aceto-nitrates described by Berl and Smith (Ber. 1907, **40**, 903; abst. J. S. C. I. 1907, **26**, 273), and prepared by them from cellulose nitrates of higher nitrogen content. Their increased reactivity with iodine, Fehling's solution and fixation of basic dyes showed the product to contain cellulose hydrates. In this connection see Ost and Westhoff (Chem. Ztg. 1909, **33**, 197; abst. J. S. C. I. 1909, **28**, 325), and C. Schwalbe (Z. ang. Chem. 1909, **22**, 197; abst. J. S. C. I. 1909, **28**, 216).

[4] F. P. 441555, 1912; abst. J. S. C. I. 1912, **31**, 955.

[5] D. R. P. 314317, 314318, 1918; abst. J. S. C. I. 1920, **39**, 122-A; Chem. Zentr. 1919, **90**, IV, 919.

According to J. Duclaux[1] nitrocellulose may be purified and recovered from substances containing it, such as old or damaged powders, waste celluloid, etc., by forming a solution, e. g., in acetone, methyl alcohol, alcohol-ether, methyl formate or acetate, or ethyl formate and either purifying the solution by dialysis or precipitating the nitrocellulose by addition of liquids which retain the impurities. The solution may be dialyzed through membranes of viscose or of cellulose precipitated from cuprammoniacal solution, or of denitrated nitrocellulose, under pressure equal to or greater than the osmotic pressure. The impurities pass through the membrane. In purifying by precipitation, the nitrocellulose may be precipitated by addition of water which may contain sulfuric acid, or sodium carbonate or by addition of organic liquids such as benzene, toluene, xylene, carbon tetrachloride, chloroform or other chlorinated hydrocarbons. A quantity of benzine or other organic liquid insufficient to produce precipitation may be added to the nitrocellulose solution, which is then precipitated by addition of water. The precipitate may be washed and boiled with water, the vapors being condensed to recover the volatile solvents.

The method of H. Wertheim[2] is for the recovery of cellulose nitrate by precipitation from celluloid solutions, and from the other materials (as camphor) contained therein. The method of pyroxylin precipitation of T. Castell[1] is somewhat analogous.

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[1] E. P. 130619, 1919; abst. C. A. 1920, **14**, 123.

[2] Aust. P. Anm. 1755, 1911. E. P. 6268, 1912; abst. C. A. 1913, **7**, 3025; J. S. C. I. 1913, **32**, 420; Chem. Ztg. Rep. 1913, **37**, 557.

In the process of J. D. for the recovery of nitrogen from cordite and its conversion into fertilizer,[2] the following procedure is recommended:

A metric ton of water is put in a shallow mixing vessel provided with a stirrer and brought to ebullition, a metric ton of lime stirred in, then 4 l. of pyridine, and then a metric ton of cordite. Shortly after, the reaction begins and in $^1/_2$ hr. the surface is covered with a layer of scum several cm. in thickness. For about an hr. at this stage the reaction requires attention, being accelerated by increasing or restrained by diminishing the heat, with stirring, after which it may be left largely to take care of itself, it being necessary only to keep the mass in the condition of a rather soft paste by adding warm water, and to keep the temperature between 85° and 95°. When by examination it appears that the hard cordite grains have disappeared the mass is evaporated, by heating for 2-3 hrs., to a very thick paste containing 16-25 parts of water, when it is put into molds and allowed to set. The total operation, charging, reaction, discharging and cleaning up ought to be completed in 24 hrs. The product appears as a coarse, brown powder, resembling brown peat, is non-inflammable, non-deliquescent and contains 6% of fixed N. A metric ton (2200 lbs.) of cordite gives $1^3/_4$ metric tons of this fertilizer. This process of conversion by lime, using pyridine as a catalyst, was developed in England and it is proposed to apply it to the 11,000,000 lbs. of surplus cordite offered by the British army for sale in France.

Uses of Nitrocellulose in the Dry State. Outside of the applications of the cellulose nitrates for smokeless powder and similar warlike purposes, the ramifications of which constitute Vol. VII of this work, the nitrocelluloses in a dry state have but few technical uses and these are relatively unimportant.

In 1877 patent protection was granted to E. Prentice[3] for the waterproofing of guncotton in order to retard its action by soaking with a solution of beeswax and "benzoline," but so far as aware no commercial application resulted from this idea. The nitrated celluloses have been used in small amounts for signaling purposes, it having been known for some time that when guncotton is fired in the open air it gives rise to a brilliant flash of light which can be seen at a great distance and does not act explosively or give rise to a loud report unless it be confined. It had been thought that inasmuch as it could be easily stored in a wet place without danger and readily dried when required for use that it was preferable to gunpowder for such purposes. However, other luminous signaling chemicals have been found more efficient. Winiwarter's patent for an improved chemical composition for making guncotton matches[1] and a soaking of the nitrocelluloses in solutions of different salts to produce colored flames and pyrotechnics[2] are unimportant.

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[1] J. Pharm. Chim. 1852, **21**, 135.

[2] Rev. prod. Chim 1919, **22**, 597; abst. C. A. 1920, **14**, 842.

[3] E. P. 2768, 1877; abst. Wag. Jahr. 1878, **24**, 466; Chem. Ind. 1878, **1**, 205. Nitrocellulose was early used by R. Boettger (Poly. Notizbl. 1873, **28**, No. 1; abst. Ding. Poly. 1873, **207**, 261; Poly. Centr. 1873, **39**, 268; Pharm. Centralh. 1873, **15**, No. 10; Chem. Tech. Mitth. 1872-3, **22**, 300; Chem. Centr. 1873, **44**, 107; Amer. Chemist, 1873, April, 397; Wag. Jahr. 1873, **19**, 355; J. C. S. 1873, **26**, 956; Jahr. Chem. 1873, **26**, 1032) in the preparation of red quick matches, cotton being nitrated in skeins, then impregnated.

Kleffel[3] made the discovery that if a glass plate is covered with collodion and after this has become solid through evaporation a printed paper is pressed upon it with the hand, an impression of the letters is left upon the collodion remaining which is readily discernible. After the complete drying of the latter while the impression is but imperfectly seen in transparent or reflected light, after breathing upon the plate, the letters being depressed, are rendered clear while the other portions remain opalescent.

A. Brock[4] endeavored to develop parlor fireworks or "balloons" in which a cylinder of tissue paper is ignited and produces a hot air current, which, when the cylinder is nearly burned away, carries it upwards, and in order to cause the "balloon" to scintillate and give off slight reports, the lower part of the paper tube was dipped in a pyroxylin solution.

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[1] Pharm. J. Trans. **12,** 143. The match composition of Courvoisier (F. P. 96530, 1874; abst. Bull. Soc. Chem. 1874, **21,** 192; Wag. Jahr. 1874, **20,** 425) contains 5.5% nitrocellulose.

[2] Segurier, Rev. Sci. **28,** 90; abst. Berz. Jahr. Chem. 1849, **28,** 350.

[3] Pharm. Ztg., Dec., 1872; abst. Am. J. Pharm. 1872, **44,** 356.

[4] E. P. 22988, 1900. A. Johnston and L. Dow (U. S. P. 34061, 1862) described the use of nitrated cloth for the manufacture of cartridges. Quite similar is the process of A. Tribe, E. P. 2073, 1884. Sudheim and Koppen (D. R. P. 7784, 1879; abst. Dingl. Poly. 1880, **236,** 88; J. Amer. Chem. Soc. 1879, **1,** 588; Chem. Tech. Rep. 1879, **18,** I, 280; Wag. Jahr. 1880, **26,** 949) manufacture friction matches by covering the tips with a mixture of nitrocellulose, copal and Canada balsam to render them water-proof. H. Pfiffard (Jahr. Chem. 1888, **41,** 2904) found that pyroxylin sprinkled with magnesium powder made a suitable flashlight preparation. X. Landerer (Wittstein's Vierteljahrschr. f. Pharm. **8,** 20; Poly. Centr. 1859, **25,** 1697) employed guncotton to ignite a large number of candles at the same time.

In the treatment of vegetable fibers to resist direct cotton colors and to increase the dyeing property of a given fiber by the same agent to produce multicolored effects in dyeing and in printing, J. Schneider[1] treats said fiber, such as cotton, with three parts of strong sulfuric acid of 1.84 sp. gr. and one part of nitric acid of 1.51 sp. gr. The fiber is thereby nitrated. However, by the addition of varying amounts of water to the nitrating mixture, the patentee claims to be able to produce nitrates upon the fiber having a decreased affinity for the direct or substantive dyestuffs and increased absorptive power to fix or retain the basic dyestuffs.

In rendering paper moisture-proof and more durable by increasing the tensile strength of the same[2] T. Fritsch causes the paper to pass through a nitrating bath whereupon it is superficially nitrated and afterwards washed to neutrality in the usual manner.

In the preparation of separators for use in a secondary galvanic battery,[3] cardboard treated with a mixture of concentrated nitric and sulfuric acids and afterwards coated with "silicate paint" or with gelatin hardened with formaldehyde is used. This process is somewhat similar to that as devized by E. Sperry,[4] who prepares vegetable fiber into a fabric for envelopes for storage batteries by first removing the oleaginous and soluble starch matter from the fiber, then drying and nitrating in the usual manner, the nitration being performed with a mixture of 113.5 parts of nitric acid, sp. gr. 1.42, and 150 parts of sulfuric acid, sp. gr. 1.84, at a maximum temperature of 78° F. After nitration the fabric is washed and treated "with a weak solution of nitrobenzol."

The cellulose nitrates being insoluble in all the gastric and enteric juices, are therefore useless as substitutes for gelatin or keratin for the preparation of capsules to inclose medicaments for internal administration.

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[1] E. P. 3645, 1907; abst. C. A. 1908, **2**, 2626; J. S. C. I. 1908, **27**, 332; Chem. Ztg. Rep. 1908, **32**, 180.

[2] E. P. 6590, 1906; abst. J. S. C. I. 1906, **25**, 1001; C. A. 1907, **1**, 777.

[3] R. Fortun and E. Semprun, E. P. 8280, 1901; abst. J. S. C. I. 1901, **20**, 777.

[4] U. S. P. 723329, 1903; abst. J. S. C. I. 1903, **22**, 560; J. A. C. S. 1903, **25R**, 494.

In the formation of a composition fuel, A. Zimmer[1] uses nitrocellulose as a binder for coke, coal or peat dust or other granular combustible material. The binder is dissolved in a solvent, which is subsequently partially or wholly evaporated. In an example stated, proportions of benzol, acetone, nitrocellulose and pitch are mixed with coal, the product being briquetted after about half the volatile matters have been evaporated. Rather expensive fuel.

In order to facilitate the lighting of candles and night-lights, the wicks are treated or impregnated with a ready inflammable material as nitrocellulose, and are then re-inforced with wax in the usual manner, the projecting end of the wick being afterwards hammered out in order to separate or fray out the several threads.[2] The wicks are either treated with a solution of nitrocellulose, or may comprize a strand of guncotton.

The waterproof cartridge case of Kynoch, Ltd. and G. Hookham[3] is concerned with the waterproofing and increasing of cohesion in paper sporting cartridge cases by the use of nitrocellulose. Whereas revolving brushes used in printing textile fabrics are usually covered with horse hair or other similar material, it has been proposed[4] to replace the hairs by long narrow strips cut from nitrocellulose photographic films. The waste clippings from film manufacture, are said to be usefully employed for this purpose.

The corneous mass of B. Herstein[5] comprizes nitrocellulose treated with alkali and then with weak acids to indurate it. The coating mass of S. v. Medveczky[6] contains small pieces of nitrocellulose (as celloidin) which are boiled in an alkali silicate until the solution is saturated with the soluble part of the celloidin, thus producing a viscid solution of value (?) in the arts.

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[1] E. P. 22834, 1910; abst. C. A. 1911, **5**, 3336; J. S. C. I. 1911, **30**, 881. The artificial fuel of the American Linseed Co. (E. P. 127585, 1919; Can. P. 187413, 1918) comprizes nitrocellulose gelatinized with methyl alcohol, bringing the colloid to the desired viscosity by the addition of 90–95% ethyl alcohol.

[2] W. Calderwood, E. P. 26955, 1910.

[3] E. P. 21844, 1898; abst. Arms and Expl. 1899, **7**, 159.

[4] Soc. Anon. des Plaques et Papiers Photographiques, A. Lumiere et ses fils, F. P. 350187, 1904; abst. J. S. C. I. 1905, **24**, 1300; J. Soc. Dyers Col. 1905, **21**, 354.

[5] D. R. P. 214193, 1907; abst. Chem. Zentr. 1909, **80**, II, 1398; Zts. ang. Chem. 1910, **23**, 384; Jahr. Chem. 1909, **62**, II, 390; Chem. Ztg. Rep. 1909, **33**, 627; Wag. Jahr. 1909, **55**, II, 555; Mon. Sci. 1913, **79**, 38.

[6] D. R. P. 239773, 1911; abst. Wag. Jahr. 1911, **51**, II, 554; Zts. ang. Chem. 1911, **24**, 2288; Chem. Zentr. 1911, **82**, II, 1501; C. A. 1912, **6**, 2186;

In the incendiary composition of A. Chanard[1] a small amount of nitrocellulose in a finely divided state is incorporated with a combustible material as resin, oil of turpentine, or heavy oil of tar, a solvent (alcohol) common to all being used. The inflammability of the mass is augmented by introducing a combustible hollow cylinder, closed at both ends, and containing a very easily inflammable liquid, such as cotton soaked in gasoline, and a fuse. It is intended as a filling for incendiary shells.

J. Kessler,[2] J. Schaub[3] and H. Brigham[4] have all recently described artificial or solidified fuels of which the nitrocelluloses constitute an essential part. In the first process, a metallic powder containing bronze powder and alcohol comprizes the formula advocated. In the second process, a cellulose nitrate soluble in methyl or ethyl alcohol is specified, while in the last process, dehydrated ethyl alcohol 92, and acetone 14 parts with 8 parts nitrocellulose constitute the formula recommended.

Preparation of Acid-Proof Nitrated Filtercloth.[5] It was R. Böttger who in 1860 first described the application of guncotton for the filtration of strong acids.[6] Patent protection for this observation, however, was made by O. Hering[7] who immersed the cloth first in concentrated nitric acid, then in strong sulfuric acid.[8] It was found, that subsequent immersion in the sulfuric acid was necessary in order to preserve the

Chem. Ztg. Rep. 1911, **35**, 568. Aust. P. 58185, 1912. U. S. P. 1012887, 1911; abst. C. A. 1912, **6**, 549.

[1] E. P. 131644, 1918; abst. C. A. 1920, **14**, 350.

[2] U. S. P. 1329610, 1920; abst. J. S. C. I. 1920, **39**, 220-A.

[3] Can. P. 187413, 1918.

[4] U. S. P. 1313876, 1919; abst. C. A. 1919, **13**, 2756.

[5] Pharm. J. Trans. **2**, 189; see also Neuste Erfind. Erfah. 1879, **6**, 557; Chem. News, 1860, **2**, 35; 1894, **70**, 38. Wilson's Cyclopaedic Photog. 1894, 91; Poly. Notiz. 1860, **15**, 97; Ann. 1860, **114**, 111; Dingl. Poly. 1860, **155**, 463; Pharm. Centralh. 1860, **2**, No. 44; Poly. Centr. 1860, **26**, 863; Chem. Tech. Mitth. 1859–1860, 134.

[6] Ann. 1860, **114**, 111; abst. Poly. Notiz. 1860, **15**, 97; Dingl. Poly. 1860, **155**, 463; J. prakt. Chem. 1860, **79**, 384; Jahr. Chem. 1860, **13**, 680; Poly. Centr. 1860, **26**, 863.

[7] Farbenfabr. vorm. F. Bayer & Co., D. R. P. 72969, 1892; abst. Chem. Ind. 1894, **17**, 464; Ber. 1894, **27**, 179-R; Zts. ang. Chem. 1893, **6**, 371; Mon. Sci. 1894, **44**, 65.

[8] Farbenfabriken vorm. F. Bayer & Co., Zts. ang. Chem. 1907, **20**, 571; abst. Wag. Jahr. 1907, **53**, I, 584.

tensile strength of the cellulose[1] which is superficially nitrated.

According to the method as developed by C. Claessen,[2] nitrated cloths for filter purposes[3] may be prepared so as to render them acid-resisting by first immersing the cloth in cold nitric acid of 40°-50° Bé., then in concentrated sulfuric acid of about 60° Bé., finally washing with water until entirely neutral. By this method a superficial nitration only is effected. Claessen has pointed out that F. Erban obviously has confined his operations to the treatment of textiles, that is woven goods, the process followed being steeping the cotton cloth for an hour in cold nitric acid at 76°-106° Tw. and then after draining, for a similar period in sulfuric acid of 142° Tw., finally washing with water until the wash water no longer had an acid reaction. Such cloths, however, have been found to speedily deteriorate by use and are unduly costly owing to the imperfect superficial nitration of the cellulose and consequently only a partial resistance to the action of the acids. Filter cloth which resists even the strongest acids, can, according to Claessen, be prepared by weaving it from artificial threads made from a pure nitrocellulose solution. Excellent results are claimed to thus have been obtained in practice.

In contradiction to Claessen the Farbenfabriken vormals F. Bayer & Co.[4] state that completely nitrated cloth can be obtained only by weaving artificial threads prepared from collodion solution and they maintain that by their process not only is a completely nitrated cloth with 12.4%-12.9% N obtained by immersion, first in nitric acid and then in sulfuric acid, but that the cloth so prepared is superior in quality to that made by weaving nitrocellulose threads, being nearly twice as strong, more durable, more resistant to acids and chlorine, and of a less open or porous character. A sample examined was found to contain only 10.9% N whereas cellulose hexanitrate requires 14.14% N and the pentanitrate 12.76% N.

H. Warren[5] has used this material with advantage for the determination of phosphates and similar precipitates susceptible to reduction by incineration. He first purifies pure filter paper to remove silica by immersion in hydrofluoric acid followed by extraction with ether in order to remove fat. The sheets of this paper are then immersed singly for five minutes in a mixture of equal volumes of nitric acid 1.5 and commercial vitriol 1.84. Paper prepared in this manner is said to filter rapidly, retain the finest precipitates such as barium sulfate and calcium oxalate, and ignite almost instantaneously. Still slower burning filters of nitrocellulose are obtained by means of a mixture of one volume of nitric acid in two volumes of sulfuric acid of the above strength. It has also been found that by the addition of a small amount of hydrofluoric acid to the nitrating mixture, the desilication of the filter occurs co-incident with the nitration.

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[1] D. R. P. 58133; abst. Zts. ang. Chem. 1891, **4**, 721; Wag. Jahr. 1891, **37**, 385; Ber. 1892, **25**, 180-R. Eschellmann, D. R. P. 107050; abst. Wag. Jahr. 1900, **46**, I, 345. D. R. P. 88681; abst. Wag. Jahr. 1896, **42**, 262.

[2] Zts. ang. Chem. 1907, **20**, 318; abst. C. A. 1907, **1**, 1462.

[3] F. Erban, Zts. Schiess. Spreng. 1906, **1**, 433; abst. Chem. Zentr. 1907, **78**, I, 382.

[4] Zts. ang. Chem. 1907, **20**, 317; abst. Wag. Jahr. 1907, **53**, I, 583; J. Soc. Dyers & Col. 1907, **23**, 175; C. A. 1907, **1**, 1169.

[5] Chem. News, 1895, **71**, 165; abst. Jahr. Chem. 1895, **48**, 1360; Bull.

E. Cramer[1] also employed filter papers consisting wholly or partly of nitrocellulose in order that incineration may be more rapid and complete. He calls attention to the fact that such papers also offer the additional advantage of filtering very rapidly and of being less hygroscopic than ordinary filter paper. In this respect they approach in properties the hardened or toughened filter papers of the market. When the filter is highly nitrated and burns too energetically a small amount of paraffin may be added to decrease the speed of ignition, and minimize the possibility of spurting of the contents during ignition out of the crucible.[2]

For filtering water, beer, wine or other beverages, C.

Soc. Chim. 1895, **14**, 914; Chem. Centr. 1895, **66**, I, 1036.

[1] Zts. ang. Chem. 1894, **7**, 269; abst. J. S. C. I. 1894, **13**, 833; Proc. Amer. Pharm. Assoc. 1895, **43**, 493; Jahr. Chem. 1894, **47**, 350. In the manufacture of acid proof fabrics for filtering purposes according to the method of Höpfner (Wag. Jahr. 1897, **43**, 1153), not the finished fabric is nitrated, but the threads. These are reeled off from a bobbin passing through concentrated nitric acid and then into strong sulfuric acid, washed and woven. To improve the strength of the fabric, asbestos, or gutta percha covered threads are woven in with the nitrocellulose.

[2] To produce solid cloths for protective purposes against acids, D. Bachrach (U. S. P. 692102, 1902; abst. Chem. Ztg. 1902, **26**, 165; J. A. C. S. 1902, **24**, 381) recommends the addition of graphite or bitumen. About 10% of either is said to produce a cloth which will successfully resist long contact with corrosive chemicals. If it is desired to blend the nitrocellulose with the graphite or bitumen an acid resisting solvent known as "picamer" (F. Greening, E. P. 22019, 1894) may be used to dissolve the nitrated cellulose. Picamer may be obtained by fractionating wood-tar distillate with chromic acid or alkaline potassium bichromate. See also the process of E. Müller, E. P. 12867, 1898.

Field,[1] impregnates cloth, canvas, paper or like medium with a solution of nitrocellulose in glacial acetic acid, and gelatinizes by subsequent immersion in water.

A pyroxylin network for use as sheaths or separators for secondary-battery electrodes is made by winding a pyroxylin thread openly on a flat mandrel in a series of layers crossing at right-angles, then dipping in a solvent so that the threads cohere, then immersing in water to remove the solvent, and finally cutting the threads along one or more edges of the mandrel.[2]

Dyeing Nitrocellulose. F. Springmühl[3] in 1872 described the preparation of colored pyroxylin solutions, in which the latter, dissolved in alcohol-ether, were combined with alcoholic solutions of dyestuffs, thus producing colored lacquers, which upon drying, formed clear, transparent films of high luster.

E. Jacquemin[4] endeavored to "animalize" cotton in order to bring its power of dyestuff receptiveness to that of silk, by superficial or incomplete nitration of the cellulose, and apparently with a considerable degree of success. The "Fernandine" process of Weil[5] had for its object enhancing the fastness of dyestuffs upon cotton by dyeing in the ordinary manner, and then increasing the resistance of the dyed fabrics to moisture and perspiration by a thin coating of pyroxylin in solution upon the colored fabrics.

P. Magnier and L. Doerflinger[6] sought to superficially nitrate flax and other filaments by a momentary immersion in the nitrating bath, washing, treating with sulfurous acid to partially "deoxidize" it, after which the cellulose may be dyed or printed upon

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[1] E. P. 17472, 1912; abst. C. A. 1914, **8**, 274; J. S. C. I. 1913, **32**, 882. See also Chem. News, 1860, **2**, 35; 1891, **64**, 85; 1896, **74**, 98.

[2] V. de Karavodine, E. P. 2493, 1911; abst. J. S. C. I. 1912, **31**, 238. He nitrates cotton thread or fabric by immersion for 5–10 minutes in a mixture of 3 parts of H_2SO_4 to 1 part HNO_3. See also E. P. 28867, 1911; abst. C. A. 1913, **7**, 2017; J. S. C. I. 1912, **31**, 285.

[3] Muster Ztg. 1872, No. 20; abst. Poly. Centr. 1872, **38**, 827; Wag. Jahr. 1872, **18**, 816. See also F. Kuhlmann (Compt. rend. 1856, **42**, 673, 711; **43**, 900, 950; J. prakt. Chem. 1856, **69**, 288; 1857, **71**, 347) was of the opinion that by spontaneous decomposition, pyroxylin which had lost a portion of its nitrogen content, absorbs dyestuffs with greater avidity, an idea to which we do not subscribe at the present time.

[4] Bull. Soc. Chim. 1874, **21**, 486; abst. Wag. Jahr. 1874, **20**, 893; Chem. News, 1874, **30**, 145; J. C. S. 1874, **27**, 1026.

[5] F. P. 98047, 1873; abst. Bull. Soc. Chim. 1874, **22**, 46; Wag. Jahr. 1874, **20**, 891.

[6] F. P. 122550, 1878; Add. of Jan. 24, 1879. E. P. 4711, 1878.

"under the most favorable conditions." Somewhat similar is the method proposed by A. Bang and C. Clolus[1] who prepare vegetable textiles to facilitate their dyeing, consisting in transforming the cellulose "into a slightly azotized product," capable especially of being dyed with colors having a nitrogenous base as the aniline dyes, soluble indigo, and litmus. In their method of procedure the cellulose textile is immersed in concentrated nitric acid for a short period, or in a mixture of nitric and sulfuric acids, and after washing to neutrality, dyed directly without mordants.

In an investigation of the chemical action of light on dyed colors undertaken by D. Brownlie,[2] twenty colors were dyed an equal shade on cotton, oxycellulose, trinitrocellulose, jute and silk, and comparisons made. No difference was observed in the fastness when dyed on cotton, oxycellulose, nitrocellulose or jute. The work of J. Schneider[3] has been along somewhat similar lines.

In the method of dyeing nitrocellulose as evolved by Farbwerke vorm. Meister, Lucius & Brüning[4] solutions are added to the nitrocotton which, with or without the addition of catalyzers or oxidizing agents, produce by subsequent oxidation, the desired color. In a typical example cited by the patentee, *p*-hydroxyphenyl-*p*-aminotolylamine 5 parts, and zapon lacquer 100 parts, are dissolved, and small traces of cupric chloride dissolved in alcohol then added.

The dyeing of nitrocellulose artificial filaments (which contain practically no nitrogen after denitration) is discussed in Vol. III, wherein is detailed the various formulas and methods for the formation of colored pyroxylin lacquers, bronzing liquids and waterproofing compositions, either for transparent (dyestuffs) to translucent and opaque (lakes and pigments) effects. (See this Vol., p. 63.)

In the dyeing of pyroxylin plastics, nearly all of the basic organic dyestuffs and many of the acid ones are applicable when soluble in methyl or ethyl alcohols, and such solutions may be added to pyroxylin in solution to form various colored effects.

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[1] E. P. 1811, 1881. F. P. 142447, 1881; abst. Mon. Sci. 1882, **24**, 729.

[2] J. Soc. Dyers Col. 1902, **18**, 288; abst. J. S. C. I. 1903, **22**, 23.

[3] J. Soc. Dyers Col. 1910, **26**, 25; abst. Wag. Jahr. 1910, **56**, II, 449.

[4] D. R. P. 285323, 1914; abst. C. A. 1916, **10**, 967; Chem. Zentr. 1915, **86**, II, 212; Chem. Ztg. Rep. 1915, **39**, 311; Zts. ang. Chem. 1915, **28**, II, 401; Wag. Jahr. 1915, **61**, II, 271. See Zts. Weiss. Mikr. 1909, **26**, 265.

Sheets which are not colored in bulk may be dipped in an alcoholic solution of the dyestuff, the depth of penetration depending on the nature of the dye, the concentration and the penetration of the pyroxylin by the solvent in which the dyestuff is dissolved. Solvents differ widely in their influence on the penetration of dyestuffs in pyroxylin masses, acetone being especially efficient in aiding penetration of basic coloring matters.

Peculiar and striking effects may be produced in dyeing sheets by means of color tests in qualitative inorganic analysis. These in general comprize a salt which is soluble in alcohol and which may therefore be incorporated with the plastic in the process of manufacture, and sheets containing this alcohol-soluble inorganic salt being either dipped in an alcoholic solution of another salt which gives a colored precipitate or color, or the sheet may be dipped in an aqueous solution of the salt which contains sufficient acetic acid (usually 15%-30%) to penetrate superficially the pyroxylin and precipitate the colored salt on and in the plastic.

Examples of such combinations are as follows: Column 1, contains the salt soluble in alcohol or other liquid solvent of cellulose nitrate. Column 2, the aqueous or acetic acid solution of the salt in which the sheet is immersed, and Column 3, the color imparted and the precipitate formed, (see next page).

If the surface of celluloid be partially colored by immersion in a solution of a dyestuff and then washed and dried, it is found that by a brief second immersion in a different-colored solution, the uncolored portion can be dyed, without the shade of the colored part being much affected, and upon this observation is based a process for preparing multicolored surfaces by direct dyeing.[1] After the second and subsequent immersions in the dyestuff solution, it is preferable to at once wash the material in a medium in which it cannot be dyed, celluloid being preferably washed in water. It is stated that this method can be applied to the preparation of three-color screen-plates.

Amorphous Nitrocellulose. It is well known that in a straight nitrocellulose smokeless powder, the acetone colloided ester has not the toughness that the same cellulose nitrate possesses when colloided with alcohol-ether, and hence is not as suitable for ballistic purposes in small arms, on account of the proneness to the development of excessive pressure from too rapid combustion in the rifle chamber.

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[1] Vereinigte Kunstseidefabriken A.-G. F. P. 305165, 1908.

1	2	3
Potassium iodide	Lead acetate	Yellow lead iodide
" "	Mercuric chloride	Deep red mercuric iodide
" "	Silver nitrate	Light yellow silver iodide
Lead acetate	Potassium chromate	Yellow lead chromate
" "	Sodium phosphate	White lead phosphate
" "	Sodium sulfide	Black lead sulfide
Silver acetate	Potassium chromate	Brick-red silver chromate
" "	Sodium sulfide	Black silver sulfide
Cochineal or carmine	Ammonia	Deep scarlet
Gold chloride (auric)	Stannous chloride	Purple of Cassius
Iron chloride (ferric)	Tannin	Black
" " "	Ammonia	Brick-red ferric hydroxide
" " "	Potassium ferrocyanide	Blue ferric ferrocyanide
" " "	Hematoxylin	Black
" " "	Salicylic acid	Purple (fugitive)
Copper acetate	Ammonia	Blue
" "	Potassium ferrocyanide	Brown cupric ferrocyanide
" "	Sodium sulfide	Black cupric sulfide
Cadmium chloride	" "	Yellow cadmium sulfide
Arsenous acid	" "	Yellow arsenous sulfide
Antimonic chloride	" "	Orange antimonic sulfide
Chromic chloride	" "	Green chromic hydroxide
Manganous chloride	" "	Pink manganous sulfide
Zinc acetate	" "	White zinc sulfide
Nickel chloride	Oxalic acid	Green nickel oxalate

Nitrocellulose may be rendered "amorphous" by the following described treatment, and when in this condition, it has been stated, may be colloided with acetone to form a powder in which the toughness of the grain compares favorably with that induced by alcohol-ether colloiding. The nitrocellulose is first dissolved to a thick jelly and placed in a mixer provided with heavy and unusually efficient agitation arrangement. When the solution is in active agitation, water is gradually added to the malaxator in a fine stream. It will be observed after the addition of a certain amount of water—this amount varying greatly with the type of nitrocellulose operated upon—the power required to operate the agitator suddenly diminishes greatly. The addition of a small amount of water beyond this point results in the complete precipitation of the nitric ester is an impalpable, structureless form, which does not agglutinate together upon pressure, and which may readily separate from the acetone-water by cloth or paper filtration. Such nitrocellulose when dried and again dissolved in acetone, is said to give a colloid which in tensile strength is nearly if not quite the equal of that induced by alcohol-ether gelatinization.

Indurating Nitrocellulose. It has long been recognized, that in order to obtain the desired and uniform ballistic effect, especially in nitrocellulose intended for large caliber guns, the powder granule must have a high tensile strength to withstand the immense pressure in the rifle chamber in order that the combustion may occur progressively within determined limits.

As early as 1882[1] W. Reid and D. Johnson patented a process for hardening grains of smokeless powder containing nitrocellulose and other nitrated bodies, 100 parts by volume of nitrocellulose being moistened with 50-80 parts ether, or methyl or ethyl alcohols, either alone or in admixture. H. Maxim[2] treats guncotton with solvents as ether or acetone in an exhausted vessel to eliminate air bubbles and compact the material. By this means, according to the patentee, a very hard and dense product is obtained.

The Indurite of C. Munroe patented in 1893,[3] also known as Naval Smokeless Powder, represents a nitrocellulose from which the lower esters were first removed by treatment with methyl alcohol, the highly nitrated cellulose being then gelatinized with mono-nitrobenzene in the proportion of about 0.9-1.8 of the former to 1 of the latter, by repeatedly passing the mass through masticating rolls until it was "colloidized" into a dark translucent mass resembling India rubber. The sheet was stripped off, cut into strips or bands, being then immersed in hot water to remove

[1] F. P. 147325, 1882. E. P. 619, 1882; abst. Dingl. Poly. 1883, **248**, 510; Chem. Ind. 1882, **5**, 101; 1883, **6**, 10; Ber. 1883, **16**, 265; Chem. Tech. Rep. 1883, **22**, I, 202; J. S. C. I. 1882, **1**, 76; Wag. Jahr. 1883, **29**, 148; Mon. Sci. 1911, **74**, 156. D. Johnston, Can. P. 24692, 1886.

[2] F. P. 194792, 1888; abst. Mon. Sci. 1889, **33**, 756.

[3] U. S. P. 489684, 1893; abst. Chem. Ztg. 1893, **17**, 135, 136; Chem. Tech. Rep. 1893, **32**, I, 235; Tech. Chem. Jahr. 1892-3, **15**, 171; J. A. C. S. 1893, **15**, 356. E. P. 580, 1893; abst. J. S. C. I. 1893, **12**, 375. Cf. J. A. C. S. 1896, **18**, 834. See, E. Worden, "Nitrocellulose Industry," 1911, **2**, 939.

the nitrobenzene. As the cellulose nitrate hardened the color lightened, and by varying the extent of incipient gelatinization, the finished product was modifiable from a brisant rupturing explosive to a slow-burning propellant.

A. Cocking and Kynoch, Ltd.[1] have described an apparatus especially designed for the hardening of nitrocellulose by solvent vapor. In the method as divulged by C. Curtis and G. Andre,[2] the cellulose ester is coated with tanno-gelatine to increase its density by a decrease in porosity.

The disruptive force required to burst a powder grain of known dimensions, density and composition, may vary within wide limits depending upon the nitrogen content of the cellulose ester and the nature and completeness with which the solvent has penetrated. The recent series of "activators" brought forward by Nobel Explosives Co., and referred to elsewhere herein, are notable examples of the "catalytic"(?) action which is exerted by minute amounts of solvents as colloiding agents in nitrocellulose induration.

Nitrocellulose may also be reduced to powder form[3] by treatment with a solvent and non-solvent as acetone and water, the compactness of the powder being varied within wide limits by the method of precipitation used. Instead of precipitating the nitrocellulose by the addition of a large bulk of water, the ester in solution, is agitated while small amounts of non-solvents are added to the point of precipitation.

Denitration of Nitrocellulose is carried on commercially primarily in connection with the preparation of nitrocellulose artificial filaments, one of the main difficulties encountered in the manufacture of artificial silk from this source being the regular production of a thread which is uniformly and sufficiently denitrated, for threads which differ in the amount of nitrogen content by 0.1% show a marked difference in their susceptibility and in their absorptive capacity for dyestuffs. H. Diamanti,[4]

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[1] E. P. 22965, 1901; abst. J. S. C. I. 1902, **21**, 1412.

[2] E. P. 843, 5821, 1891; abst. J. S. C. I. 1892, **11**, 456; Chem. Centr. 1892, **63**, II, 279; Chem. Ztg. 1892, **16**, 1320; Chem. Tech. Rep. 1892, **21**, I, 224; Wag. Jahr. 1892, **38**, 377; Tech. Chem. Jahr. 1891, **14**, 139.

[3] A. Luck and C. Cross, E. P. 5286, 1898; abst. J. S. C. I. 1899, **18**, 400.

[4] E. P. 17460, 1907; abst. J. S. C. I. 1907, **26**, 1275; J. Soc. Dyers Col. 1908, **24**, 118. F. P. 378143, 1906; abst. J. S. C. I. 1907, **26**, 1136; Mon. Sci. 1910, **73**, 298.

Fremy,[1] L. Bergier,[2] P. Vieille,[3] H. Richter,[4] H. Turgard,[5] P. Cazeneuve,[6] D. Woodmann,[7] A. Bernstein,[8] A. Petit,[9] C. Häussermann,[10] F. Wislicki,[11] H. de Chardonnet,[12] H. Diamanti, P. Loisif and H. Champin,[13] E. Weston,[14] together with the Societe Anonyme pour l'etude Industrielle de la Soie Serret[15] have devised methods for accomplishing the denitration of cellulose filaments on a commercial scale.[1] E. Bindschedler[2] has disclosed ways for the utilization of old denitration baths; while A. Dulitz[3] and W. Mitscherling[4] have contributed to this art. Inasmuch as the denitration of cellulose to-day is carried out almost entirely in conjunction with the formation of artificial filaments to reduce the inflammability thereof, this topic will be taken up more in detail under that subject in Volume IV of this series.

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[1] F. P. 203191, 1890; abst. Mon. Sci. 1890, **35**, 766.

[2] F. P. 349134, 1904; abst. J. S. C. I. 1905, **24**, 617; Chem. Zts. 1905, **4**, 209; Mon. Sci. 1907, **67**, 600; J. Soc. Dyers Col. 1906, **21**, 182.

[3] Mem. poud. salpetres, 1907-8, **15**, 61; abst. Zts. Scheiss. Spreng. 1911, **6**, 181; C A. 1910, **4**, 961.

[4] E. P. 12695, 1901; abst. J. Soc. Dyers Col. 1902, **18**, 232; J. S. C. I. 1902, **21**, 1038. F. P. 312040, 1901; abst. Mon. Sci. 1902, **58**, 104. D. R. P. 125392, 1901; abst. Jahr Chem. 1901, **54**, 895, Mon Sci. 1902, **58**, 145; Wag. Jahr 1903, **49**, II, 417; Chem. Centr. 1901, **72**, II, 1139. D. R. P. 139442, addition to D. R. P. 125392; abst. Wag. Jahr. 1904, **50**, II, 388. D. R. P. 139899, addition to D. R P 125392, 1901; abst. Jahr. Chem. 1903, **56**, 1019; Wag Jahr. 1903, **49**, II, 388, 417; Chem. Centr. 1903, **74**, I, 860. Aust. P. 13163 S. Coulier, Belg. P. 210951, 1908.

[5] U S. P. 508124, 1893, abst Chem. Tech Rep. 1893, **32**, II, 163; Chem. Ztg. 1893, **17**, 1772; J A. C. S. 1893, **15**, 712.

[6] F. P. 346693, 1904, abst. J. S. C. I. 1905, **24**, 194; Mon. Sci. 1907, **67**, 599. For the reducing action of ammonia on nitrocellulose, see J. Spiller (Chem. News, 1866, **12**, 296; Bull Soc. Chim 1868, (2), **5**, 227; Chem. Centr. 1866, **37**, 45; Jahr. Chem. 1865, **18**, 596), E. Guignet (Rep. Chim. Pure, 1863, **5**, 114), A Béchamp (Rep. Chim. Pure, 1863, **5**, 289).

[7] J. A C S. 1892, **14**, 112, abst Chem. Centr. 1892, **63**, II, 401; Jahr. Chem. 1893, **41**, 2734, Proc. Amer. Pharm. Assoc. 1893, **41**, 441; J. S. C. I. 1892, **11**, 839; cf. Chem. Ztg. 1892, **16**, 163; Dingl Poly. 1892, **283**, 88, 137.

[8] D. R. P. 232373, 1910; abst. C. A. 1912, **6**, 1853; Kunst. 1911, **1**, 154; Chem. Ztg Rep. 1911, **35**, 230. D. R. P. Anm B-57875, 1910. For the denitration of nitrocellulose with lactic acid, consult E. Berl and R. Klaye, Zts. Schiess. Spreng. 1907, **2**, 403; abst Chem Zentr. 1908, **79**, I, 1381.

[9] U. S. P. 665975, 1901; abst. J. A. C. S 1902, **24**, 52. E. P. 15343, 1900; abst. Mon. Sci. 1903, **59**, 283; J. Soc Dyers Col. 1900, **16**, 267.

[10] Chem. Ztg. 1905, **29**, 420; abst Jahr. Chem. 1905-8, II, 981; Wag. Jahr 1905, **52**, II, 398; Ber. 1904, **37**, 1624.

[11] F. P. 427694, 1911; abst. Mon. Sci 1913, **79**, 19.

[12] E. P. 5270, 1888; abst. J. S. C. I. 1889, **8**, 474. F. P. 221488, 1892; 231230, 1893; abst. Mon. Sci. 1893, **42**, 85; 1894, **44**, 64. E. P. 10858, 1915; abst. C. A. 1917, **11**, 214; J. S. C. I. 1916, **35**, 302. F. P. 410652, 1909; abst. Chem. Ztg. Rep. 1910, **34**, 301; Mon. Sci. 1913, **79**, 73. Cf. Compt. rend. 1889, **108**, 961; Jahr. Chem. 1889, **42**, 2840. F. P. 478404, 1914; abst. C. A. 1916, **10**, 2307; J. S. C. I. 1916, **35**, 1009. D. R. P. 46125; abst. Chem. Centr. 1889, **60**, I, 656; Jahr. Chem. 1889, **42**, 2840; Mon. Sci. 1905, **62**, 321; Tech. Chem. Jahr. 1888, **11**, 527; Chem. Tech. Rep. 1889, **28**, I, 81; Industriebl. 1889, 166; Ber. 1888, **21**, 913; Jahr. Chem. 1888, **41**, 2860.

[13] F. P. 378143, 1906; abst. J. S. C. I. 1907, **26**, 1135; Mon. Sci. 1910, **78**, 298. D. R. P. 217128; abst. Wag. Jahr. 1909, **55**, II, 391; 1910, **56**, I, 97. Belg. P. 201695, 1907. Aust. P. 42740.

[14] U. S. P. 264987.

[15] F. P. 369170, 1906; abst. C. A. 1908, **2**, 1363; Mon. Sci. 1910, **73**, 298. G. Gorrand, F. P. 354424, 1905; abst. C. A. 1907, **1**, 1076; Mon. Sci. 1906, **65**, 167; J. Soc. Dyers Col. 1905, **21**, 286. E. P. 6166, 1906; abst. C. A. 1907, **1**, 643. Soc. Anonyme de Soie Artif. de Tubize, F. P. 358987, 1905; abst. C. A. 1907, **1**, 1064; Mon. Sci. 1906, **65**, 169; J. Soc. Dyers Col. 1906,

Nitrates of Hydrocellulose and Oxycellulose. These bodies have probably never been prepared in a pure state, interest chiefly lying in the influence which they exert upon the stability of the nitrocellulose. In 1895[5] E. Ungania described the preparation of explosives of nitrocellulose mixed with paraffin, nitromannite and inorganic salts. Previous to this had appeared the processes of A. Luck and A. Durnford[6] and C. Lundholm and J. Sayers[7] for the manufacture of granulated explosives in which

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22, 112. See also Cie. de la Soie de Beaulieu, D. R. P. 217128, 1907; abst. Chem. Zentr. 1910, **81**, I, 313; Zts. ang. Chem. 1910, **23**, 384; Chem. Ztg. Rep. 1910, **34**, 75; Wag. Jahr. 1909, **55**, II, 391; J. Soc. Dyers Col. 1910, **26**, 90.

[1] See L. Vignon, Compt. rend. 1900, **131**, 520; abst. Bull. Soc. Chim. 1901, **25**, 130; Chem. Centr. 1900, **71**, II, 891; 1901, **72**, I, 440; J. C. S. 1900, **78**, i, 589, 629. P. Magnier and L. Doerflinger, E. P. 4711, 1878. See also W. Green, E. P. 9879, 1889. "Denitration of Pyroxylin," Chem. Ztg. 1905, **29**, 420.

[2] Chem. Ztg. 1909, **33**, 174; abst. C. A. 1909, **3**, 1327, 1927; Chem. Zentr. 1909, **80**, I, 1276. See also P. Heermann, Mitt. kgl. Materialsprufungsamt, 1910, **28**, 227; abst. Chem. Zentr. 1910, **81**, II, 343; J. S. C. I. 1910, **29**, 939.

[3] Chem. Ztg. 1910, **34**, 989; abst. J. Soc. Dyers Col. 1910, **26**, 251; Jahr. Chem. 1910, **63**, II, 429; C. A. 1911, **5**, 2176; J. S. C. I. 1910, **29**, 1151. Belg. P. 17259, 1903. See also R. Valette, E. P. 20637, 1904; F. P. 344660, 1904; abst. J. S. C. I. 1904, **23**, 1212. C. Dow, D. R. P. 153671. Knöfler, D. R. P. 88556, 1894. F. P. 247855, 1895.

[4] Kunst. 1912, **2**, 308; abst. C. A. 1912, **6**, 3185; Wag. Jahr. 1912, **58**, II, 444. For weakening of artificial silk due to faulty denitration, see S. Culp, Färb. Ztg. 1909, **21**, 141; abst. C. A. 1910, **4**, 3006.

[5] E. P. 12325, 1895; abst. Chem. Ztg. 1896, **20**, 975; Mon. Sci. 1897, **50**, 81; J. S. C. I. 1896, **15**, 376.

[6] E. P. 4769, 1895; abst. J. S. C. I. 1896, **15**, 135; Chem. Centr. 1896, **67**, I, 1150; Chem. Ztg. 1896, **20**, 652.

[7] E. P. 6399, 1889; abst. Dingl. Poly. 1890, **278**, 20; J. S. C. I. 1890, **9**, 414; Tech. Chem. Jahr. 1890–91, **13**, 153. E. P. 12338, 1889; abst. J. S. C. I. 1891, **10**, 573. E. P. 13486, 1889; abst. J. S. C. I. 1890, **9**, 893; Wag. Jahr. 1890, **36**, 546. D. R. P. 53296; abst. Zts. ang. Chem. 1890, **3**, 556; Chem. Centr. 1891, **62**, I, 647; Chem. Ztg. 1890, **14**, 1266; Chem. Tech. Rep. 1890, **29**, II, 145; Wag. Jahr. 1890, **36**, 540; Ber. 1891, **24**, 182-R; Tech. Chem. Jahr. 1890–91, **13**, 162. D. R. P. 55650; abst. Zts. ang. Chem. 1891, **4**, 469; Chem. Ztg. 1891, **15**, 567; Chem. Tech. Rep. 1891, **30**, I, 219; Chem. Ind. 1891, **14**, 335; Wag. Jahr. 1891, **37**, 428; Ber. 1891, **24**, 429-R; Mon. Sci. 1891, **38**, 655; Meyer Jahr. Chem. 1891, **1**, 332.

nitrated substances derived from hydrocellulose and oxycellulose were mixed with camphor and oxidizing agents.

A. Girard[1] has converted hydrocellulose into the nitrated derivative, and has found that hydrocellulose nitrates in much the same manner as does cellulose, but the nitrohydrocellulose formed is very friable, nitrates more readily and decomposes with greater facility. Girard commented on their friability and increased solubility as being properties peculiarly advantageous for photographic collodions, a point to which we do not subscribe at the present day.

The hydrocellulose of R. Stahmer[2] when nitrated[3] passes into solution as a reddish brown liquid, from which water precipitates a nitro-compound with a bright ivory-like surface. H. de Chardonnet has described a "hydrate of nitrocellulose"[4] differing from ordinary nitrocellulose in having in its composition a quantity of water of "condensation," and alleged to be especially adapted to the formation of artificial filaments.

According to C. Cross and E. Bevan,[5] when gelatinous oxycellulose is washed with strong nitric acid until free from water, and then diffused through a mixture of strong nitric and sulfuric acids, quickly passes into solution. This solution after standing about an hour then poured in a fine stream into a large volume of water, precipitates the "nitro" body as a white flocculent mass, which upon drying at 110°, gave 6.48% N and a formula corresponding to $C_{18}H_{23}O_{16}(NO_2)_3$.

L. Vignon[6] has nitrated hydro- and oxycellulose and found that the viscosity of their ether-alcohol solutions to be much less than the normal cellulose nitrates. They are equally inflammable, show a greater affinity for basic dyestuffs, and are less stable. They reduce Fehling's solution on boiling, that of nitro-oxycellulose more energetically, and below the boiling point, potassium hydroxide of 1.3 density slowly attacks both products, that from oxycellulose more rapidly. When distilled with HCl both nitrated bodies gave off great quantities of nitrous fumes, and the distillate in each case showed the presence of furfural—more so with the oxycellulose compound.

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[1] Compt. rend. 1879, **89**, 170; abst. J. C. S. 1989, **36**, 911.

[2] See this volume, p. 132.

[3] E. P. 19039, 1900; abst. J. S. C. I. 1901, **20**, 926; J. Soc. Dyers Col. 1901, **17**, 295.

[4] E. P. 24638, 1893, abst. J. S. C. I. 1895, **14**, 33. See also E. P. 2211, 1886; 1656, 5376, 1890; 19560, 1891; abst. J. S. C. I. 1887, **6**, 139; 1891, **10**, 359, 566; 1892, **11**, 939. Compare I. duVivier, E. P. 2570, 1889; abst. J. S. C. I. 1890, **9**, 286. U. S. P. 455245.

[5] J. C. S. 1883, **43**, 23; abst. Ber. 1883, **16**, 415; Chem. News, 1882, **46**, 240; J. S. C. I. 1884, **3**, 206, 291; Bull. Soc. Chim. 1883, **39**, 671; Chem. Ind. 1883, **6**, 353; Chem. Tech. Rep. 1883, **22**, II, 94; Dingl. Poly. 1883, **250**, 280; Jahr. Chem. 1883, **36**, 1366, 1777; Mon. prod. Chim. 1883, 242.

[6] Compt. rend. 1898, **126**, 1658; 1900, **131**, 509; 1903, **136**, 818, 898; abst. Bull. Soc. Chim. 1901, **25**, 130; Compt. rend. 1898, **127**, 872; J. S. C. I. 1900, **19**, 1039; 1903, **22**, 572. See also J. C. S. 1895, **67**, 84; 1904, **85**, 336. For action of KOH on oxynitrocellulose see L. Vignon, Bull. Soc. Chim. 1899, **21**, 597.

Extensive researches of the higher nitrates of cellulose, hydrocellulose and oxycellulose have been made by E. Berl and R. Klaye[1] who prepared hydro- and oxycellulose in various ways and nitrated them under different conditions.[2] Their results are shown in the following table:

Nitrated Compound	% N (Nitrometer)	% N (Dumas)	Solubility in Ether-Alcohol	Fixation of Methylene Blue Mgm. per Gm	Viscosity (Relative)
Cellulose	13 5	13 32	1 8	0 6	10,000
Hydrocellulose	13 23	13 36	12 15	2 4	65 7
H_2O_2: Hydralcellulose	13.07	.....	22.5	2.4	8 13
$KMnO_4$: Oxycellulose	13 31	.. ..	18 0	1 6	5 15
Br.Oxycellulose	12.92	13.29	15.5	3.5	9.06
$Ca(MnO_4)_2$.Oxycellulose	13.25	.....	20.5	3.3	11.10
HNO_3: Oxycellulose	12.87	13.28	34.0	5.0	7.94
$KClO_4$: Oxycellulose	13.04	.....	18.0	3 0	7.2

The general conclusion was drawn that the formation of either or both hydro- and oxycellulose nitrates must play a comparatively minor part in the formation of higher cellulose nitrates at ordinary nitration temperatures.[1]

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[1] Zts. Schiess. Spreng. 1907, **2,** 381, 403; abst. C. A. 1908, **2,** 184; J. S. C. I. 1907, **26,** 1157; J. C. S. 1908, **94,** i, 504; Chem. Zentr. 1908, **79,** I, 1381; Chem. Ztg. Rep. 1908, **32,** 43; Jahr. Chem. 1905–08, II, 976.

[2] The products were then nitrated at 19°–20° for 24 hours in an acid of the composition: H_2SO_4 (46.22%), HNO_3 (42.03), N_2O_4 (0.25), and H_2O (11.50%). The proportion of acid to material was 50 to 1. The nitrates were washed with cold and then hot water for a prolonged period and eventually dried in a vacuum desiccator at 33°–40° over phosphorous pentoxide. A complete analysis was made in a special combustion tube and the nitrogen determined both by the nitrometer and by Dumas' method. The viscosity was determined in a Cochius viscometer with a 2% acetone solution. Experiment showed that the nitration of oxycellulose is complete in 24 hours. Prolonged immersion up to 144 hours does not increase the nitrogen content. The following conclusions are drawn. Under similar conditions the highest nitrates are obtained with pure cellulose. Cellulose, oxycellulose and hydrocellulose are dyed more readily by methylene blue than the corresponding

L. Vignon has shown[2] that the action of KOH on oxynitrocellulose results in the formation of oxypyruvic acid, m. pt. 204°.

Xyloidins are the amorphous products resulting from the action of nitric acid on the polysaccharides, in distinction to guncotton, pyroxylin and the collodions, which are made by the action of a mixture of nitric and sulfuric acids.[3] The xyloidins should not be confounded with the xyloidine of Braconnot. Excluding the starch nitrates, the xyloidins may be classified as follows: *Group 1.* The products obtained by warming wood- or cotton-fibers, filter paper, "hydralcellulose" (acid-cellulose lactone) or pyroxylin with nitric acid of sp. gr. above 1.4, until the substance is dissolved, and pouring the solution into water or into strong sulfuric acid. *Group 2.* Products obtained by dissolving loose cotton-wool in cold nitric acid of sp. gr. 1.47, and allowing the solution to stand, or diluting it with water. Spun or felted fibers are changed by this treatment, but are not dissolved like loose cotton. *Group 3.* Products obtained by dissolving cotton in concentrated sulfuric acid at a low temperature, and adding strong nitric acid, keeping the temperature low. When washed and dried, all these xyloidins are white, amorphous, but not homogeneous powders. They differ widely in their solubility relations and nitrogen contents. The reaction between cellulose and nitric acid depends so largely on the temperature, and the concentration of the acid, and is accompanied by the production of such variable amounts of by-products soluble in water, that the yields and properties of products made in the same way may vary considerably. The xyloidins are all com-

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nitrates, and the nitrates of oxycellulose and hydrocellulose more easily than cellulose nitrate itself. Increase of nitrogen in cellulose increases the viscosity in acetone solution, and the viscosity of the nitrates of oxycellulose and hydrocellulose is very much less than that of the corresponding cellulose nitrate solutions.

[1] Cf. E. Knecht, Ber. 1904, **37**, 549. C. Piest Zts. ang. Chem. 1907, **21**, 2497. See also Proc. Amer. Pharm. Assoc. 1894, **42**, 1200; West. Druggist, 1894, 98.

[2] Compt. rend. 1898, **127**, 872; abst. Chem. News, 1899, **79**, 35. See also the topics Hydrocellulose, this vol., p. 127, and Oxycellulose, this vol., p. 164.

[3] Xyloidine is also the name applied to a yarn prepared from ribbons of paper unwound from spools by a differential motion which twists the ribbons as they are unwound. H. Stevens, Paper and Pulp, 1905, **10**, 656; abst. . S. C. I. 1905, **24**, 1250.

pounds of nitric acid, but whether they are all true esters, or whether some of them are merely adsorption compounds, has not yet been decided. On treatment with alkali hydrosulfides, the xyloidins of Groups 1 and 2 yield "acid-cellulose" in the form of a hydrated jelly. Collodion cotton and guncotton when dissolved in warm concentrated nitric acid are not actually decomposed, but undergo changes with the result that the amorphous products obtained on dilution differ considerably from the amorphous colloids formed by the action of organic solvents. The product of the ordinary nitration of Girard's hydrocellulose differs from the xyloidins, in the fact that its organized structure is preserved, and the amorphous starch nitrates differ from the cellulose xyloidins in that they yield soluble starch or dextrin when denitrated. It is unlikely that the xyloidins will attain immediate industrial importance as explosives, their cost of production being greater than that of the pyroxylins, while they are characterized by lack of uniformity and by instability on storage. It has, however, been proposed to utilize products which occupy an intermediate position between the ordinary pyroxylins and the xyloidins.[1]

C. Haeussermann has found[2] that when 10 gm. of cotton wool are treated with 2 k. of nitric acid (sp. gr. 1.473) at 10°–12°; the honey-like mass produced, is allowed to stand for 24 hours at the ordinary temperature, filtered through guncotton, and poured into water. The xyloidin which separates, is washed free from acid and dried. It forms a white powder, with a somewhat greenish tinge, which decomposes at 195° with a slight explosion, but when ignited in the air burns, fairly rapidly but quietly. It dissolves gradually in glacial acetic acid, but only swells in acetone and ethyl acetate. The product obtained by treating it with sodium hydrosulfide or ammonium hydrosulfide, dissolves while moist almost completely in a 10% solution of sodium hydroxide, but can be reprecipitated from the solution by acids, salts and alcohol; it also exhibits the other characteristic properties of acid-cellulose.[3]

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[1] C. Haeussermann, Zts. Schiess. Spreng. 1908, **3**, 121, 305; abst. J. S. C. I. 1908, **27**, 918; Chem. Zentr. 1908, **79**, I, 2024; II, 1021; Zts. ang. Chem. 1910, **23**, 1761; Jahr. Chem. 1910, **63**, II, 423.

[2] Zts. Schiess. Spreng. 1906, **1**, 39; abst. J. S. C. I. 1906, **25**, 444; Chem. Centr. 1906, **77**, I, 1196; Jahr. Chem. 1905–8, II, 979.

[3] G. Bumcke and R. Wolffenstein, Ber. 1899, **32**, 2493; abst. J. S. C. I. 1899, **18**, 940.

The product obtained by denitrating a xyloidin richer in nitrogen, prepared by precipitating with water a clear solution of guncotton in 40 times its weight of nitric acid (sp. gr. 1.5) is also found to be acid-cellulose. Collodion-cotton and guncotton dissolve in nitric acid of sp. gr. 1.473 at the ordinary temperature, but only very slowly and not completely.

H. Jentgen[1] has investigated the action of nitric acid alone upon cellulose, and has studied the conditions of the reaction upon the properties of the xyloidin formed.

The nitric acid used should be within the density limits of 1.469-1.479, for above and below these limits the cellulose goes into solution with great difficulty. The temperature should be held below 25°. From the treatment as outlined above of cellulose a viscous solution is formed from which a cellulose nitrate of 7.6%-8.8% N is precipitated by the addition of water. The product either swells or dissolves in acetone, alcohol-ether and amyl acetate. Soluble in hot glacial acetic acid, partially in acetic anhydride, ethyl acetate and mixtures of acetic and sulfuric acids. The length of nitration apparently has but little effect upon the solubility of the product, a period of 2.5 hours producing the most satisfactory results. The product takes the form of corneous masses or translucent, harsh-feeling fibers. Xyloidin is less stable than the pyroxylins or collodions, and is readily attacked by concentrated HCl.

E. Knecht has shown[2] that when cotton is placed for 15 minutes in pure nitric acid of 82° Tw. and then washed, and dried, considerable contraction of the fiber results, and the material increases in weight and tensile strength. More dilute acid tenders and weakens it. Analysis shows that partial nitration of the fiber has taken place, and its behavior towards direct cotton dyestuffs—from which baths it takes a three or four times deeper shade than ordinary cotton—points to the fact also of mercerization. The author contends, that inasmuch as it does not dye with basic colors, no oxycellulose has been formed. The use of strong nitric acid for stripping colors and for mercerizing is advocated.

Cellulose Nitrites. According to P. Nicolardot and G.

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[1] Zts. ang. Chem. 1912, **25**, 944; abst. C. A. 1912, **6**, 2524; J. C. S. 1912, **102**, i, 416; Chem. Zentr. 1912, **83**, II, 244.

[2] J. Soc. Dyers Col. 1896, **12**, 89; abst. J. S. C. I. 1896, **15**, 449; Chem. Tech. Rep. 1896, **35**, 232; Wag. Jahr. 1896, **42**, 999.

Chertier,[1] when viscose silk is treated with nitrous gases in the presence of nitric acid (sp. gr. about 1.5) a mixture of the nitrous and nitric esters of cellulose results from which the former may be separated from the latter by means of acetone in which they are insoluble. The nitrites of cellulose thus obtained are said to be gray in color, gelatinous when moist, very brittle when dried, and insoluble in water, alcohol, ether, acetone, chloroform or ethyl acetate. They lose nitrogen to an appreciable extent at the ordinary temperature, and more quickly on heating, giving yellow, friable, extremely acid products.

Water effects hydrolysis slowly at the ordinary temperature and completely after 12 hours' boiling, and the same takes place in the cold with hydrochloric, nitric or sulfuric acids, although acetic acid attacks these esters but incompletely at 50°. In their presence, methyl and ethyl alcohols are oxidized to the corresponding aldehydes, and even to acids. The authors allege that nitrous esters are prone to occur, under certain conditions in nitrocellulose prepared from cotton, and cause rapid deterioration. When they are present, lower results are obtained in the determination of nitrogen with the nitrometer than with Schloesing's method, because the nitrites are at once decomposed by sulfuric acid.

The experimental evidence adduced by the above authors has been called in question by M. Marqueyrol and D. Florentin,[2] who point out the existence of cellulose nitrites, as above described, are doubtful for the following reasons: (a) It is improbable that nitrous esters could be formed in a nitric acid medium. (b) It is well known that nitrated celluloses with a low nitrogen content are insoluble in the usual solvents for guncotton, namely, ethyl acetate, acetone, etc. (c) Various investigators have shown that the nitric esters of cellulose when saponified with aqueous or alcoholic alkali give rise to considerable quantities of nitrite, since reduction accompanies the saponification.

It is furthermore shown that if cellulose is nitrated by the prolonged action of nitric acid (D_4^{15} = ca. 1.5) to which excess of carbamide has been added to destroy all the nitrous acid present, or formed during the reaction, products are obtained which cannot be nitrous esters, but which nevertheless possess the properties ascribed to these compounds by Nicolardot and Chertier.

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[1] Compt. rend. 1910, **151**, 719; abst. Chem. Zentr. 1910, **81**, II, 1888; J. C. S. 1910, **98**, i, 818; C. A. 1911, **5**, 1588; J. S. C. I. 1910, **29**, 1299; Bull. Soc. Chim. 1911, **9**, 856; Jahr. Chem. 1910, **63**, II, 423; Meyer Jahr. Chem. 1910, **20**, 328; Zts. Schiess. Spreng. 1911, **6**, 354.

[2] Bull. Soc. Chim 1911, (4), **9**, 306; abst. J. C. S. 1911, **100**, i, 355; C. A. 1911, **5**, 3229; J. S. C. I. 1911, **30**, 532; Rep. Chim. 1911, **11**, 461; Chem. Zentr. 1911, **82**, I, 1687.

Cellulose Sulfuric Esters. In 1869 W. Gintl observed[1] that when pyroxylin is thoroughly moistened, with concentrated sulfuric acid, after having been rendered neutral by previously washing with water, the pyroxylin gradually dissolves and is converted into a colorless, viscous syrup. Little attention, however, has been paid to these observations by subsequent workers.

In 1891 C. Cross, E. Bevan and R. Jenks[2] investigated a number of mixed esters of cellulose, such as the acetobenzoates, and nitrobenzoyl nitrates and conclude from the results obtained that under treatment with mixtures of nitric and sulfuric acids, the cellulose hydroxyls react with both negative radicals yielding nitrosulfuric esters. The maximum fixation of sulfuric acid as determined by them, was 4-6 parts with bleached cotton, and 1.9-4.2 parts with unbleached cotton, the percentages being calculated on the weight of the original cellulose. They found that the essential condition most favorable to the retention of the sulfuric residues in combination, is found to be short duration of exposure to the action of the mixed acids. The presence of the mixed esters in the products purified by exhaustive washing, was verified by treatment with diluted acetone, in which these products are soluble.

C. Hake and R. Lewis[3] have studied the formation of sulfuric esters in the nitration of cellulose, and their influence on stability,

[1] Wien. Akad. Ber. **59,** II, 809; J. prakt. Chem. 1869, **107,** 478; Zts. Chem. 1869, **12,** 703; Jahr. Chem. 1869, **22,** 753; Poly. Centr. 1870, **36,** 159; Chem. News, 1869, **20,** 323, Chem. News Amer Reprint, 1870, **6,** 115; Bull. Soc. Chim. 1870, **13,** 435; Wag. Jahr. 1870, **16,** 220; Allgem Oesterr. Apotheker Verein. 1869, 421; Chem. Tech. Rep. 1869, **8,** II, 98; Amer. Pharm. Assoc. 1870, **18,** 270.

[2] Ber. 1901, **34,** 2496; abst. J. S. C. I. 1901, **20,** 1133; Chem. News, 1901, **84,** 61; J. C. S. 1901, **80,** i, 672; Bull. Soc. Chim. 1902, **28,** 130; Chem. Centr. 1901, **72,** II, 882; Jahr. Chem. 1901, **54,** 892; Wag. Jahr. 1901, **47,** I, 501; Meyer Jahr. Chem. 1901, **11,** 316.

[3] J. S. C. I. 1905, **24,** 374, 914; abst. Chem. Centr. 1905, **76,** I, 1170, 1702; J. C. S. 1905, **88,** i, 512; Jahr. Chem. 1905-8, II, 975; Meyer Jahr. Chem. 1905, **15,** 357. It would appear that the sulfuric acid esters are merely transition bodies which pass on into the nitric esters. The longer, within reasonable limits, the cotton is left in contact with the acids, the more complete will probably be the conversion into nitric esters.

with a view of determining the causes which are responsible for the deterioration of explosives containing guncotton. They attribute the deterioration to the presence of sulfuric esters of cellulose derived from the latter by replacement of hydroxyl groups by the group $-SO_4H$, and draw the conclusion that sulfuric acid combines chemically with cellulose during nitration to form esters which decompose into esters of a more stable character, partly by hydrolysis during washing (especially in the presence of small amounts of mineral acids), and partly during storage of the finished product. According to these authors, the difficulty of eliminating these esters explains the erratic behavior observed in explosives exposed to tropical climatic conditions.

C. Cross, E. Bevan and J. Briggs[1] found with the cellulose aceto-sulfates that under the action of cold, distilled water alone, the sulfuric acid residue of these esters was gradually split off, much more rapidly, however, in boiling water, whereas on treatment with alkaline solutions the whole of the acetic acid residue could be eliminated by saponification, while the combination between the cellulose and sulfuric acid remained intact in the form of a cellulose sulfuric ester. The reason for this anomalous behavior appears from the fact that the sulfuric residue in these esters probably is in the form $-SO_4H$, readily hydrolyzable by the action of water and acids, but becomes SO_4M in the presence of alkalis, and these combinations are singularly stable.

On account of the fact that a larger proportion of sulfuric acid may be made to combine in conjunction with the acetic acid radical than with nitric acid, it has been possible to study the aceto-sulfates more comprehensively than with the corresponding nitro-sulfates. Their investigations illustrated the relatively great stability of the combination between cellulose and sulfuric acid towards alkaline saponifying agents, and its extreme sensitiveness towards acid reagents, including water. The observations of R. Robertson are recorded in the next chapter in connection with the practical stabilization of nitrocellulose.

The method of determining the SO_4 radical as adopted by

[1] Ber. 1905, **38**, 1859, 3531; abst. J. S. C. I. 1905, **24**, 685, 1251; J. C. S. 1905, **88**, i, 512, 862; Chem. News, 1905, **92**, 70; Bull. Soc. Chim. 1906, **36**, 638, 639; Rep. chim. 1905, **5**, 414; Chem. Centr. 1905, **76**, II, 36, 1625; Chem. Ztg. Rep. 1905, **29**, 178; Jahr. Chem. 1905–1908, II, 986; Meyer Jahr. Chem. 1905, **15**, 357; Wag. Jahr. 1905, **51**, II, 399.

Hake and Lewis was to saponify with caustic soda, add sodium carbonate, and after evaporation to dryness and ignition, to dissolve in HCl and precipitate with barium chloride. As checked up by C. Kullgren,[1] this method leads to erratic and low results, it being difficult to precipitate barium sulfate in the presence of large amounts of alkali salts without the probability of error. Kullgren recommends the decomposition of the nitrocellulose with HCl, evaporating to dryness, followed by ignition in a current of oxygen, absorbing the sulfur oxides on alkali coated quartz grains. The salts are then dissolved from the quartz, the oxidation completed by the addition of a small amount of sodium peroxide, and the sulfate precipitated with barium chloride, as before.

Sulfonic esters of cellulose are prepared according to a patented method[2] by the treatment of alkali cellulose prepared from bleached cotton by the action of zinc chloride and hydrochloric acid, with toluene-*p*-sulfonyl chloride in the presence of 10% aqueous NaOH. The toluene-*p*-sulfonic ester of cellulose separates after 20 hours as a white, amorphous powder insoluble in zinc chloride solution or in cuprammonium solution, dissolves in hot glacial acetic acid, and forms transparent pellicles when evaporated from solutions of epichlorhydrin, chloroform or ethyl acetate.

In order to ascertain the effect of combined sulfuric acid on the stability of nitrocellulose, C. Piest[3] has determined the SO_4 in 12 samples of stabilized nitrocellulose, and the stability of each by four different methods. The sulfate content was found to vary from about 0.02%–0.06% SO_3 and showed no relation to stability. It was found, however, that those samples having the greatest amount of SO_3 were the highest in ash, from which he infers that the SO_3 present is primarily derived from the sulfates in the wash water. To determine the SO_3, Piest heats 20 gm. nitrocellulose with 70 cc. HNO_3 (sp. gr. 1.4) and 1 gm. KNO_3 to dryness on the steam bath, ignites carefully, dissolves the residue containing the SO_3 as K_2SO_4 in dilute HCl, and precipitates with $BaCl_2$. Other investigators, as appear above, found much larger amounts of combined sulfuric acid in nitrocellulose.

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[1] Zts. Schiess. Spreng. 1908, **3**, 146, 201; 1912, **7**, 89; abst. C. A. 1908, **2**, 3147; 1912, **6**, 1366; J. C. S. 1908, **94**, i, 768; 1912, **102**, ii, 682; J. S. C. I. 1912, **31**, 303; Chem. Zentr. 1908, **79**, I, 2024; II, 231; 1912, **83**, I, 1399; Jahr. Chem. 1905–1908, II, 974; Wag. Jahr. 1908, **54**, I, 442; 1912, **58**, I, 444. For solubility of cellulose in sulfuric acid, see E. Berl, F. P. 454754; Hung. P. Anm. B-6377; abst. Chem. Ztg. 1913, **37**, 653 Z Ostenberg (see p. 95) and the International Cellulose Ester Co. (Can. P. 176178) dissolve cellulose in a mixture of sulfuric and hydrochloric acids, while R. Willstätter (D. R. Anm. W-42345, 1913; Aust. P. 80118, 1914) prefers concentrated HCl (see p. 93). The process of M. Boullier (F. P. 319217, 1902) is similar.

[2] Akt. Ges. für Anilin Fabrikation, D. R. P. 200334; abst. J. C. S. 1908, **94**, i, 955; Chem. Zentr. 1908, **79**, II, 655; Zts. ang. Chem. 1908, **21**, 2233; Jahr. Chem. 1905–8, II, 987; Wag. Jahr. 1908, **54**, II, 363; Chem. Zts. 1908, **7**, 909.

[3] Zts. ang. Chem. 1913, **26**, 661; abst. C. A. 1914, **8**, 573; Chem. Zentr. 1913, **84**, II, 2184; Meyer Jahr. Chem. 1913, **23**, 363; Wag. Jahr. 1913, **59**, I, 457; Zts. Schiess. Spreng. 1914, **9**, 12.

A. Herve has called attention to the fact[1] that nitrocellulose prepared for the manufacture of celluloid contains small proportions of sulfuric acid combined in the form of esters and not removable by simple washing. This sulfuric acid is retained as a relatively stable combination in the presence of bases, when it reacts as an ester salt but is progressively eliminated by hydrolysis on boiling with dilute mineral acids. For the determination of the combined sulfuric acid, 5 gm. of the fully washed and dry nitrocellulose are boiled under a reflux condenser for 8 hours with 250–300 cc. of water containing 1 cc. of strong hydrochloric acid (sp. gr. 1.18). The nitrocellulose is filtered off, the filtrate and washings are concentrated to 150 cc. and the sulfuric acid precipitated as barium sulfate. The percentage of sulfuric acid fixed varies with the proportion of that acid used in the nitrating mixture. With a constant proportion of about 19% of water, the following results were obtained: ratio of HNO_3 to H_2SO_4 1 : 1, 0.0505% sulfuric acid fixed in the nitrocellulose; ratio 1 : 2, 0.2025%; ratio 1 : 3, 0.4290%; ratio 1 : 4, 1.34%; ratio 1 : 5, 1.81%. This combined sulfuric acid has a strongly depressing influence on the stability test of the nitrocellulose and of the celluloid prepared from it, but it is not the only factor. Compounds of low degrees of nitration or of oxycellulose or hydrocellulose also affect stability; these are most easily eliminated by boiling with alkaline water, so that effective stabilization demands both acid treatment for the sulfuric esters and basic treatment for the inferior nitrated products. This combination of conditions may be produced by boiling the nitrocellulose with a readily dissociable salt, such as 0.1%-1.0% of its weight of magnesium chloride, for about 12 hours. Satisfactory products are thus obtained which withstand the Abel heat test for 60 minutes.

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[1] Mon. Sci. 1918, **85**, 193, 241; abst. J. S. C. I. 1918, **37**, 718-A; C. A. 1919, **13**, 186, 516; Chem Zentr. 1919, **90**, II, 297, 622.

There is no doubt but what sulfuric acid adversely affects the stability of the nitrocellulose, and as a rule, it has been found that a more readily purifiable product results from the esterification of cellulose in the presence of little or no sulfuric acid. Especially is this seen in the formylation and acetation of cellulose, where the sulfuric acid, must be reduced to small amounts in order to produce esters of proper stability and desirable solubility and viscosity.

Nitrated and Chlorated Guncotton. A number of methods have been proposed and processes brought forward for combining nitrocellulose with other bodies in order to produce new and desirable results. The majority of these processes consist in impregnating the nitrocellulose with alcoholic or aqueous solutions of the materials in question, the nitrocotton being afterwards reduced to the dry state. The "chlorated guncotton" of S. Mackie, C. Faure and G. Trench;[1] the "bichromated nitrocellulose" of J. Davey,[2] and the nitrocellulose potassium triamid of C. Blondeau[3] are examples.

It has been maintained by some that the actual impregnation of nitrocotton by (say) potassium nitrate in solution, and the subsequent evaporation of the water, results in the formation of a compound having different and superior properties to the mechanical mixture of the two components.

The salts which are especially suitable for admixture with guncotton in order to supply additional oxygen are potassium, ammonium and sodium nitrates. Lead nitrate has been forbidden for this purpose in some countries on account of the deleterious fumes evolved on combustion. The total combustion of nitrocellulose and potassium nitrate corresponds to the equation:

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[1] E. P. 2742, 1876, 198, 1877; abst. Ber 1876, **9**, 205, Bayer Ind. u. Gewerbebl. 1876, 141; Dingl Poly. 1876, **221**, 94; Deut. Industrieztg. 1876, 228; Wag. Jahr. 1876, **22**, 480.

[2] E P. 2832, 1877; abst. Ber. 1878, **11**, 1390; Chem. Centr. 1878, **49**, 640; Wag. Jahr. 1878, **24**, 466.

[3] J. prakt. Chem. 1864, **93**, 320; Compt. rend. 1864, **58**, 1011; abst. Instit. 1864, 195; Chem. Centr. 1865, **36**, 44; Jahr. Chem. 1864, **17**, 569. See also Compt. rend. 1865, **61**, 378; Bull. Soc. Chim. 1865, **3**, 145; J. prakt. Chem. 1865, **95**, 189; **96**, 64; Industrieztg. 1865, 388; Dingl. Poly. 1865, **178**, 147; Chem. Centr. 1865, **36**, 997; Poly. Centr. 1865, **31**, 1597; Mon. Sci. 1864, **6**, 564; Instit. 1865, 299; Jahr. Chem. 1865, **18**, 595; Chem. Tech. Rep. 1865, **4**, II, 116. Cf. Mon. Sci. 1865, **7**, 898; abst. Wag. Jahr. 1865, **11**, 412.

$$10C_{24}H_{18}(NO_3H)_{11}O_9 + 82KNO_3 = 199CO_2 + 41K_2CO_3 + 96N_2 + 145H_2O$$

or 828 gm. (42%) potassium nitrate per 1143 gm. (58%) cellulose nitrate.

Layout and Construction of Modern Guncotton Plant. In the earlier days of nitrocellulose manufacture, special buildings were not set aside for this manufacture, and it was not sufficiently recognized that the production of guncotton and the less explosive cellulose nitrates called for special factory design and equipment, to successfully meet conditions not arising in the manufacture of gunpowder.

The chemical engineering involved in the erection and maintenance of a guncotton plant, involves the coördination of a large number of details in order that the individual steps in manufacture may synchronize to the end that the maximum output of satisfactory material with the minimum of effort, equipment and floor area may be assured. In the following suggested generalities, numerical statements, for the sake of uniformity, are based upon the rated production of 5000 pounds finished nitrocellulose per 24-hour day of three 8-hour shifts, and allowing a six-day week, with a 20% leeway for apparatus continually out of commission.

Site and Topography. In the selection of a site for the erection of a nitrocellulose plant, points to be taken into careful consideration are proximity to raw materials supply, expecially cotton and nitric and sulfuric acids; transportation facilities for employees and materials; location in an isolated, preferably woody, and sparsely settled region where the normal increment of habitation appears to ensure but little settlement in the immediate future; abundant supply of suitable water; rolling and hilly ground to permit of handling materials, especially acids, by gravity; good sewage for acid water; a large tract of ground so as not to endanger adjoining property, and preferably a location where the annual rainfall is not unduly high and where the proportion of damp and foggy days are low. A sandy soil is preferable, and location on deep rock strata should, if possible, be avoided on account of the danger of propagation to great distances, the effect of an explosion.

Climate. The plant, if possible, should be located in a mild climate on account of the long, exposed steam lines, long distances for hauling on uncovered trucks; the ready maintenance of constant temperatures in dry houses; and the difficulties encountered in placing the plant in operation in winter. About the only counterbalance is the facility of solvent recovery in cold weather, and the fact that in a cold, dry atmosphere the nitration process usually proceeds more satisfactorily and with a smaller percentage of losses by fuming. The nitrating units should be so erected as to take advantage of the prevailing winds of the locality for the dispersion of acid fumes.

Water. The amount of water required in the various processes of nitorcellulose purification will average from 12 to 20 gal. per lb. material produced, in addition to which is the water required for steam purposes and for refrigeration. A low permanent hardness in the water is undesirable, but the presence of salts like magnesium which form soluble sulfates is not deleterious. The presence of undue amounts of iron in the water is objectionable if the nitrocellulose produced is to be used for pyroxylin lacquers or for transparent plastics, and for the latter the organic matter (humus) in solution is exceedingly important as influencing the "whiteness" of the finished cellulose nitrate or acetate. The water storage tower, preferably erected on the highest point of the property as determined from the topographical map should also be located as near the source of supply as possible to reduce cost of pumping, pipe line maintenance, and installation costs.

Topographical Survey. Immediately after acquiring title to a site, a topographical survey should be made, preferably at not greater than 20 feet distances each way, and a contour map constructed therefrom. From this the levels of the entire tract are obtained, and the location of the power plant and the several buildings determined so as to take advantage to the fullest of gravity fall, and the ready transportation of materials from one building to another.

Sewage. Where riparian rights are involved in the discharge of effluents, or the potability of the discharge source may be affected, or discharge into streams or tributaries may possibly be in contradiction to the Fish and Game Commission regulations rigidly enforced in some localities, the economical disposal of sewage is a matter of prime importance. There being practically no impurities in suspension, and no coloring matter in solution, the problem is one of neutralization.

Where supplies of limestone are located near by, filtration through a bed of calcium carbonate frequently renewed, has proven efficient, the precipitated calcium sulfate but partially clogging the mass, while the calcium nitrate, being water-soluble, readily passes away. With limestone delivered at $1.75 per ton of 2000 lbs., the cost of neutralization in one factory using this method, has averaged 0.18 cents per pound of nitrocotton produced, the above being the average figure for 18 consecutive months.

Power. It is advantageous to locate the power house at the lowest point central to the plant, which makes a semi-circular layout desirable to reduce length of pipe lines. Seldom does a water power plant supply the electrical power, unless the latter be purchased. Steam is required for the boiling tubs, cotton driers, poachers, and nitrocotton dry houses, and sometimes for the blenders, and this steam constitutes four-fifths of the boiler capacity of the power house. A 2000 h. p. boiler capacity for heating and pumping, and 1000 h. p. for electric power, of 3-phase 480 volts, 60-cycle is ample. In case the electrical power is purchased, the power plant will consist only of boilers and the hydraulic pumps and fire pumps, together with the pumping system to boiling tubs, poachers, etc.

About 950 h. p. (depending on the season of the year) is required for drying the cotton, preliminary boiling, heating beater water and poacher water, running hydraulic dehydration, heating the dry houses, and heating the buildings in winter.

The electric power required in horse power is approximately as follows: for cotton picker, 25; cotton conveyor, 10; cotton dryer, 25; nitrating centrifugals if electric driven, 50; four beaters, 350; preliminary wringer, 30; general pumping, 100; poachers (12 of 10 h. p. each), 120; dehydrating wringers, 40; electric lighting, 125.

Construction of Buildings. For buildings in which nitrocotton is being manufactured, it is considered best practice to have the walls as well as the roof of light construction in the event of an explosion. The nitrating houses and the power plant are usually constructed of brick, while for the other buildings, corrugated iron sheets attached to the usual 2" x 4" or 4" x 4" uprights, and with roof of similar material have been found satisfactory. The care in construction of the building will, of course, vary with the severity of the climate.

The rules governing the construction of danger buildings as outlined by H. M. Inspectors of Explosives, A. R. 1909, p. 5, are as follows:

"The lining of a danger building need not necessarily be of wood. 'Neat' cement, i. e., cement free from sand, or any other suitable material may be used. In fact, in very dusty buildings a lining which can be effectively washed down by means of a hose has many advantages.

"The floor should be of soft material, such as wood or asphalt, free from grit; care being taken to fill up all interstices and crevices in which explosive dust may accumulate. Doors should open outwards and, while any one is in the building, should only be secured in such a manner as to be opened easily by a push. There should be plenty of them, and so far as practicable they should face towards the path by which a work-person would naturally endeavor to escape.

"(1) In working buildings, from which all the explosive is removed on completion of the day's work, the more flimsy the construction the better. In view of the distances to which heavy masses of debris have been thrown by explosions, the soundness of the principle is obvious. The actual material recommended is match-boarding, corrugated iron, or sheets of light fire-resisting material. For roofing, slates and tiles are dangerous, and tarred felt carries fire, so that only corrugated iron and fireproof sheets remain, and there are objections to these; in fact a good roofing material for working buildings containing explosives is much wanted.

"(2) In magazines, on the other hand, where explosive is present at all times, but where as a rule it is contained in securely closed packages, the chief danger to be anticipated is from unauthorized entry, and a substantial construction of brick, masonry or concrete is called for. An exception to this is made in the case of a factory where a watchman is always present at night, on Sundays, and during holidays, in which case a reasonably stout corrugated iron is allowed."

The buildings usually comprehended in a plant for a daily production as previously stated, include:

1. Cotton and General Stores House, including railroad track scale.
2. Cotton Picker House.
3. Cotton Dry House, including the storage of the dried cotton until desired for nitration.
4. Cotton Nitrating House, with accompanying acid tanks, acid weighing building, and enclosed pumping facilities, the oleum tanks having steam connections for thawing in cold weather.
5. Preliminary Boiling and Beating House of ample size.
6. Poaching, Hydro-extracting, Straining and Blending House, usually one building.
7. Storage for hydro-extracted nitrocotton pulp.
8. Alcohol-dehydration Press Building, with the accompanying housing for the accumulator, and provision for rectification of the aqueous alcohol resulting from the process.
9. Nitrocotton Dry House.
10. Laboratory, Office, Drafting Department. Telephone, Fire Alarm and Watchman Clock.
11. Steam and Electrical Power Plant.
12. Carpenter, Plumbing, Tin-smith, Lead-burning and Painting Shop.
13. Piping systems, air, steam, hot and cold water, acid and hydraulic lines, alcohol control, and Watchman shanties.

It is customary in a smokeless powder plant to arbitrarily divide the buildings into the guncotton group and the powder section, the buildings just mentioned comprizing the former section.

Lighting. In the preliminary boiling, poaching and hydro-extraction buildings, lighting through louvres in the roof in addition to lateral lighting is efficient, but in those areas where dry nitrocellulose is stored and handled attention should be directed to the fact that ignition has occurred from the focusing of the sun's rays by means of a sheet of glass containing an imperfection, the flaws undoubtedly forming lenses which concentrated the light and heat of the sun by focusing. For this building, so-called prism glass, consisting of a series of parallel lines tending to disperse the light rays, have been found to give satisfaction and eliminate this possibility of danger. Painting the windows or affixing curtains thereto has been found less satisfactory, for the paint may wear off or become rubbed, while the operator may neglect to draw the curtains.

For artificial lighting, electricity is now almost universally employed. Incandescent electric lamps, enclosed in a glass bowl, the wiring being all in piping, and the connections as far as possible located outside the buildings, is a method which has proven entirely satisfactory.

It has been experimentally ascertained that gunpowder and also finely powdered nitrocellulose will fire if the globe of an incandescent electric light be broken in an atmosphere containing such dust in suspension, hence the necessity of protecting the lamp by an outer glass globe, and this latter by a strong copper wire cage. The outer glass globe should be provided with an inlet and outlet tube for admitting a circulation of air, the capacity of the outer globe being such as to ensure that the temperature therein shall not become greater than 50°. In unusually dusty and dangerous localities, the outer globe may be so arranged as to contain water instead of air, and a circulation of water maintained. In all instances where complete globes are used, one side should be painted to obviate the possibility of the focusing of heat rays.

Lead wires should be enclosed in either metal tubing or piping up to the lamps, and the lamp wires should be soldered to the leads, each lamp being provided with a fuse cut-out outside the magazine. The fuses should consist of 0.035-0.04-inch tin wire, additional wires in parallel being provided when necessary. Each lamp should be provided with a double-throw switch outside the magazine, by means of which the circuit may be broken, and the magazine lighting system should include an efficient leakage detector and lightning arrester. The potential difference between any two points in the circuit should not exceed 110 volts.

Where electric lighting is not available as in the case of magazines, lamps containing candles of rape oil have been used, the lamps being so mounted in recesses of the walls that they can be opened from the outside of the building only. For portable lights, hand electric flash lights are probably best.

Cotton Area. The cotton storage sheds, either a portion of the general stores, or a separate building, should be of capacity for at least 60 days' supply, and 30 days' supply should be continually maintained. This is a frame and corrugated iron building, cement floor and not heated. The cubical contents of the bale (pressure to which it has been subjected) will determine the size of the cotton storage, and this varies greatly in different countries (see p. 583).

The cotton picker house is a one-story building, with addition or lean-to for motors and exhausters, of frame construction, corrugated iron covered, and heated. Concrete floor. In addition to the pickers, contains exhaust fan (36″), tin circular cotton conveyor and scales. The cotton conveyor discharges to the cotton dry house. Automatic sprinkler system and good ventilation is necessary.

The cotton dryhouse is of fireproof construction, equipped with automatic sprinkling system and should be well ventilated. In addition to the drying system, several hundred tin cans for storage of cotton in amounts equivalent to one nitrating batch should be provided, together with adequate storage capacity for full and empty cans. An ample tin lined storage bin for cotton is desirable. In one form of construction, the dry house is of two stories, the air heated to 100° being forced up and through the cotton from below. Three steel plate blowers, engine driven, with heating coils sufficient to ensure a uniform temperature not lower than 95° should be installed.

The cotton dryhouse may with advantage be connected with the nitrating house by means of a platform on which runs an industrial track for conveying the cans of weighed and cooled cotton to the nitrators.

Cotton Nitrating Area. The nitrating building of brick, concrete or hollow tile, with brick floor containing asphalt, hydrex,[1] or several layers of butt-jointed, acid-proof felt, and efficient ventilating system, is a one-story building where pot, centrifugal or displacement system of nitration is used, or three stories where the mechanical system of nitration has been installed, or a fourth floor, where the vertical motor is installed separately. Abundance of fire escapes with plenty of exits thereto. Plenty of windows. The equipment comprizes the nitrators, means for heating and cooling the entering nitrating acid, and wooden containers for drowning the nitrated cotton.

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[1] Anon , Zts. Schiess. Spreng. 1914, **9,** 248; abst. C. A. 1914, **8,** 2949. H. Coningham, Home Office Rept. 1915, **214,** 6; abst. C. A. 1915, **9,** 2502, J. S. C. I. 1915, **34,** 688. W. Curphey, Chem. Trade J. 1917, **61,** 117; abst. C. A. 1917, **12,** 3386. E. Davidson, E. P. 12233, 1910; abst. J. S. C. I. 1911, **30,** 272; C. A. 1911, **5,** 2919. A. Desborough, J. S. C. I. 1904, **23,** 560. B. Dunn, B. E. Acc. Bull. 35, abst. C. A. 1917, **12,** 2044. Escodeca, Compt.

In the acid storage, which consists of a series of cylindrical steel boilers in a concrete cradle, containing strong nitric, concentrated sulfuric, waste acid, oleum, and acid mixture ready for use, vary in capacity from 10000-100000 lbs. and should be protected from the sun by means of a shed or at least a roof, it having been demonstrated that the sun on a hot day decomposes the nitric acid with the evolution of sufficient nitrous acid to affect the result of nitration. A waste acid egg is usually located in a concrete pit, from which the acid may be pumped to one of several tanks at will. A satisfactory flooring for the nitrating house consists of acid-proof bricks laid without mortar or other cement, there being poured in a mixture of high melting paraffin and beeswax. The walls of the building may be constructed of plaster over wire, and this coated with the paraffin-wax mixture. It is hardly necessary to mention that all plaster and concrete should be of quartz or trap rock and not contain limestone on account of acid action.

The acid mixing house—a one-story building usually—frame and corrugated iron construction and heated, contains the acid mixing tank set on scales, and provided with stirring arrangement driven by 10 h. p. motor. The acid piping consists of 3″ to 5″

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rend. 1848, **27**, 158. E. Gad, Oeust. Chem. Ztg. **27**, 166; abst. C. A. 1910, **4**, 1234. W. Graff & Co, D. R. P. 201393, 1906; abst. C. A. 1909, **3**, 2376; Chem. Zts. 1908, **7**, 1001. A. Hamilton, J. Amer. Med. Assoc 1917, **68**, 2445; abst. C. A. 1917, **12**, 2043. C. Hexamer, Proc. Nat. Fire Protec. Assoc. 1916, 257; abst. C. A. 1916, **10**, 2149. W. Macnab and E. Ristori, Ber. 1895, **28**, 1018. R. Scheuffgen, U. S. P. 1118952, 1914; abst. C. A. 1915, **9**, 244. Petroelum, **4**, 927; abst. C. A. 1909, **3**, 2376. Pharm. J. Trans. **4**, 136. Compt. rend. 1848, **27**, 264. Mon. Phot. 1862–1863, **2**, 100; 1869–1870, **9**, 147; 1878, **17**, 60; Chem. News, 1864, **9**, 274; 1866, **14**, 180; 1867, **16**, 86, 113; 1871, **24**, 131. Phot. Work, 1892, **1**, 234. Ann. d'Hyg. Pub. Med. Legale, 1891, (3), **44**, 271 Photography, 1892, **4**, 616. Anthony, Phot. Bull. 1892, **23**, 580. Ann. Rep. H. M. Inspect. Expl. 1900, 23, 212. C. A. 1913, **7**, 1610.

cast iron, joints being metal to metal, flanged tested to 100 lbs. pressure, and acid valves as previously described (see p. 1468). A 50000-lb. capacity mixing tank, takes care of a 40000-lb. mix nicely. The acid tanks require 30-lb. air pressure for transference of acid expeditiously. With ideal natural gravity fall, the original nitrating acid flows to the weighing tank, thence by gravity to the nitrating house, being pumped only when the spent acid in the sump is elevated to the level of the storage tank system. Where sulfuric acid of 60° Bé. is used, the tanks are lead-lined.

Nitrocotton Stabilizing Area. A natural fall from the acid storage tanks to the acid scale house and nitrators, thus permitting gravity supply is desirable, but not necessary if acid pumps are installed, while it is also advantageous to locate the boiling tubs at a lower level than the nitrators, and thus be able to convey the purified nitrocotton from the pulper to the poacher by gravity. This should require a fall from the acid tanks to poachers of about 75 feet for efficient working. A slight grade to facilitate trucking of the product from poachers would also be advantageous.

From the drowning tubs in the nitrating building—one of which will take care of the contents of two centrifugals—the nitrocotton is either forked out into wooden trucks and pushed over manually or mechanically to the preliminary boiling house, or an automatic bucket arrangement may be used. If the latter is employed, the material from the drowning tubs is flowed to a sump where it is picked up by means of an endless belt and bucket arrangement, carried to the boiling house and there dumped into waiting trucks where it is wheeled to any desired boiling vat. A circular boiling tub 9′ x 7′, allowing for a 6″ false bottom, will accommodate a charge of 1800 lbs. nitrocotton. Preliminary boiling capacity should be calculated on the basis of 10 days' output of nitrocotton, i. e., a 5000-lb. plant should provide boiling capacity for 50000 lbs. at one time. The tanks are constructed of 3″ cypress, iron hooped. The boiling house is two stories, of frame and corrugated iron, heated, the tubs being mounted on piers, with plank trucking between tubs. The floor is of concrete. The operation of a factory may start with the boiling tubs not being under cover, and the building erected afterwards.

In the pulping operation, this is either carried on in a separate portion of the same building as the preliminary boil, or in a separate building connected by a covered platform. The pulping building is frame, of corrugated iron, heated. Hard maple floor, with concrete foundations under beaters. Hot water tank installed for supply of water to beaters.

Poaching is taken care of in a building separate from the boiling and beating, and of the same general construction, centrifugal pumps carrying the material from beater to poacher. The usual size of poacher is 10′ diameter, 7′6″ deep, provided with propellor type agitators, driven through bevel gears on shaft with tight and loose pulleys. Tubs of 3″ cypress. Floor, hard maple. Concrete sedimentation basin under the tubs mounted on concrete piers. The poaching building requires in addition, dehydrating centrifugals with bottom discharge, lead lined blending bin, scales, wooden shovels, blending tank with agitator and boxes for storage of nitrocotton.

In the alcohol dehydrating, a frame and corrugated iron building heated is desirable, but with wooden floor covered with linoleum, and walls lined inside with galvanized beaded siding, with soldered joints. The vertical, hydraulic, dehydrating cylinder press contains water cylinders above and below, is bronze lined, casting of steel At least 8 automatic alcohol measuring tanks should be provided, and 3 cylindrical tanks 4′ x 16′ for aqueous or spent alcohol, together with the requisite piping alcohol to presses, and presses to weak alcohol storage The receiving alcohol tanks are usually of 500-gal. capacity, and there should be a drop from the alcohol storage to the alcohol dehydration buildings. The weak alcohol storage tanks are conveniently of 15000 gal. each.

In the drying the nitrated cellulose after centrifugalization subsequent to blending, there is required shelf space calculating that a screen 2′ x 3′ will comfortably hold 10 lbs. of material, and that 15 such screens is about the comfortable limit for height. Therefore, 2′3″ x 3′3″ floor area will accommodate about 150 lbs. nitrocotton at one time, based on the dry weight. From this the capacity of the dryer may be calculated, due allowance being made for aisles.

Nitrocotton Storage. O. Guttmann[1] has described improvements in buildings intended for the manufacture and storage of explosives and applicable to nitrocotton storage, which consists in a concrete or porous brick construction, the roof consisting of a wooden principal, but having stretched on both the upper and lower side, sheets of expanded metal, wire netting or similar material. On the lower side a lining of matched boarding may be placed, and the roof then covered in the usual way with sheets of zinc. The patentee claims that such expanded metal is not readily perforated by falling debris, but the impact is taken up by the whole of the metal, somewhat similar to a wire mattress. The idea is intended to obviate the tendency of heavy pieces of debris and machinery falling upon the building crushing it.

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[1] E. P. 4094, 1909; abst. J S. C. I. 1910, **29**, 375; Arms and Expl. 1910, **18**, 54. See also J. S. C. I 1908, **27**, 669, Zts. Schiess. Spreng. 1908, **3**, 266.

A guncotton store house should be of fireproof construction, light roof, not heated and with hard maple floor.[1] Owing to the dangerous nature of nitrocellulose when in the *dry* state, and especially when finely pulped, the same precautions in storage should be observed as with the so-called *high* explosives.

It is expedient that these dry houses be classed as danger buildings and treated as such. Therefore they should be surrounded by an earth mound reaching to the roof, so as to deflect the force of the explosive wave upwards in event of an explosion. The entrance through the mound should, if possible, be directly opposite the door of the building. The floor of the building should be covered with oilcloth, or better, with sheet lead, the sheets of which have been joined by burning, and the sheets carried up to at least a foot above the floor on the walls at each side. The floors should be kept scrupulously cleaned by careful brushing and occasional mopping. All windows are to be made of frosted glass, all doors open outwards, the doors being locked when the building is unoccupied, and provided with a spring catch only, when workers are inside. The workers should wear all wool clothes provided with no pockets, and should carry with them no metallic articles as buttons or jewelry. Danger buildings being located in the proscribed or "clean" area, no one should be allowed to enter unless they don special rubber shoes provided there for that purpose. As explosives are easily electrified, it is advizable that a few copper nails should be placed in the sole and heel of the workers' shoes, so as to *earth* the wearer. This is especially important when handling dry, finely powdered (pulped) nitrocotton.

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[1] J. C. S. 1868, **20**, 559. Eng. Min. J. **88**, 328; abst C. A. 1909, **3**, 2872

No one should be allowed to enter the building except those duly authorized, or except in the presence of the person in whose charge the explosive is placed, and the latter should be responsible for the strict observance of all the prescribed safety regulations. All who enter should be carefully searched, and matches, other easily combustible articles, or iron or steel articles should be removed. The shoes should be carefully cleaned on a mat provided for that purpose, and magazine rubber overshoes placed on the feet of each person.

When guncotton is to be examined in a magazine, canvas should be placed on the floor that any falling dust may collect upon it, and at the close of the examination the canvas should be carefully folded from the outside inwards, taken outside and there carefully dusted. An inventory list showing the contents of each magazine should be readily accessible and open to inspection to any authorized party. The guncotton as received should be visually examined carefully, and the appearance of the package noted as to the presence of any grit, dirt or other extraneous matter, a permanent record being kept of all such examinations, together with the distinguishing marks on the individual packages. A sample of each shipment submitted to storage should be kept and these periodically examined for any indications of approaching instability.

Packages which are used for explosives a second time should be examined to see if their condition as to strength and freedom from impurity is such as to warrant their re-use, and all former marks obliterated.

C. Bichel[1] has illustrated and described a proposed method of concrete construction for explosives buildings of moderate size, in which the entire building is covered over with earth except one side for light. Each building is surrounded by a massive earth wall, entrance being by means of tunnels, the openings of which are likewise protected by heavy walls. The advantages claimed for this type of building are (1) dangerous heavy pieces of debris cannot be thrown in case of *explosion; (2) lightning protection is unnecessary; (3) the entire building is fireproof; (4) danger from falling debris from a nearby explosion is limited.* The effect of dampness is not stated, although it must be considerable.

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[1] Zts. Schiess. Spreng. 1910, **5**, 182; abst. C. A. 1910, **4**, 2880; Meyer Jahr. Chem. 1910, **20**, 326; Wag. Jahr. 1910, **56**, I, 500.

The Societe d'Etudes Chimiques l'Industrie[1] have described a process for preventing danger of explosion by adding to nitrocellulose or other porous material with the explosive, hydrazoic acid, thus tending to diminish danger of handling.

Ventilation of Nitrocotton Storage Magazines. It is important that magazines containing nitrocellulose, like those containing gunpowder, should be properly and thoroughly ventilated. Where stored in damp magazines, the cellulose nitrate may become moldy or otherwise deteriorated, and its ballistic value thereby correspondingly reduced. With nitrocellulose smokeless powders, the temperature of the magazine is not without influence on the muzzle velocity. For instance, it has been ascertained that powders tested in summer weather and used in target practice in winter gave lower velocities, and conversely. Corrections for variation in velocity due to the above have been determined and plotted. The humidity and temperature of magazines are, therefore, of considerable moment where the material is stored therein for long periods. It is a generality with the majority of nitro explosives that an abundant circulation of air should be maintained, so that in the event of incipient decomposition, the fumes would be automatically dispersed, and a cumulative effect thereby be prevented, or at least minimized.[2] In order to prevent condensation, the circulating air should always be maintained above

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1. E. P. 130166, 1919; J. S. C. I. 1919, **38,** 742-A. See also Anon, Elec. World, 1916, **67,** 433; abst. C. A. 1916, **10,** 857.

2. H. Coningham, J. S. C. I. 1911, **30,** 1335, 1470. A. Cooper-Key, Spec. Rept. H. M. I. Expl C. C.; abst. C. A. 1912, **6,** 804. H. M. Inspect. Expl Rept. No. 1919, **235;** abst. C. A. 1919, **13,** 1391. E. Bouchard-Praceiq, D. R. P. 211866; abst. Jahr. Chem. 1909, **62,** 389; Wag. Jahr. 1909, **55,** I. 430. Fabrik Explosionssicherer Gefasse, D. R. P. 266097; abst. C. A. 1914, **8,** 2248; Chem. Ztg. Rep. 1914, **38,** 144; Wag. Jahr. 1913, **59,** I, 120. E. P 6327, 1912; abst. C. A. 1913, **7,** 2998. R. Kaiser, D. R. P. 207741; abst. Wag. Jahr. 1909, **55,** I, 430. Martini & Hüneke Maschinenbau-Akt. Ges, D. R. P. 283696, 1912; abst. C. A. 1915, **9,** 3363; Chem. Ztg. Rep. 1915, **39,** 215; Wag. Jahr. 1915, **61,** II, 261. T. Rosenthal, Chem. Ind. 1912, **35,** 444, abst. C. A. 1912, **6,** 2839. J. Thomson, J. S. C. I. 1905, **24,** 690. Mechan. Mag. **26,** 192, 207, 225; abst. Eng. **12,** 148, 156, 161; Quart. J. Sci. **8,** 494. Eng. **92,** 463; abst. C. A. 1912, **6,** 153.

the dew-point, and frequent hygrometric and psychrometric determinations should be made.

This may be effectively accomplished by either keeping the air in the magazine above the dew-point by passing it over heated steam coils aided by a fan to stimulate circulation; by arranging air-shafts with revolving hoods to face the wind, and thereby conduct a large volume of air through the dry-house; or, by opening the doors and windows to the outside air, whenever the atmospheric conditions of temperature and moisture are favorable. The natural method of air regulation by means of ventilation is effected by means of a thermometer placed inside and located near a window that it may be read from the outside, and psychrometers placed outside the magazine, but protected from the sun, wind and rain. Details of procedure are contained in Volume VII of this series.

Lightning Protection. All magazines carrying considerable quantities of nitrocellulose should be protected from lightning. Much controversial has been written as to the efficiency of the ordinary lightning conductor, in which the lightning is supposed to obediently follow the various turns and twists of the conductor, and finally harmlessly disseminate itself in the ground. In the United States and some parts of Europe, fierce thunder storms are of frequent occurrence at certain seasons of the year, while in England they are less prevalent. It has been suggested that the best method of protecting storage magazines from lightning is to construct them entirely of metal, extending the sides down to moist soil, or else connecting them well in a number of places. Another suggestion put forward consists in covering completely the building with strong wire netting, or running a number of large iron wires along all ridges and edges, with groups of wires radiating from the corners, the entire system being efficiently grounded.[1]

Dangers in Connection with the Nitration of Cellulose. With the exception of the infrequent explosions of cotton dust in the cotton drying operations, fuming off in the nitration, and the possible drying of the nitrocotton instead of alcohol dehydration, there is practically no danger in the process of manufacture as a whole for the reason that the majority of the steps in purification are carried on in the presence of a large excess of water, and the probability of an explosion thereby reduced to a minimum, although it is conceivable that a particle of guncotton may explode when struck by a heavy weight, even when wet. Once it has been immersed in water in any container where the water is frequently changed, then the nitrated cotton is no longer subject to *sudden* decompositions during the subsequent steps in manufacture, but the acid and other extraneous products contained therein must be eliminated, or a *gradual* decomposition will subsequently ensue.

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[1] A description of the various forms of apparatus designed for the protection from lightning of buildings containing explosives is contained in Spreng. Waffen. Munitions, **2**, 254; abst. C. A. 1907, **1**, 2826. See also von der Hagen, Spreng. Waffen. Munitions, **6**, 162; abst. C. A. 1911, **5**, 2556. Chem. Ind. 1912, **35**, 480; abst. C. A. 1912, **6**, 3524.

The compression of guncotton into cartridges requires considerable care—more so than with gunpowder—as this is done in the warm state, and guncotton, even when cold is more sensitive than gunpowder.

Among the more important precautions to be observed in the conversion of cellulose into nitrate, are the following:

1. The cotton should be carefully freed from resin, fat and other impurities.

2. In the drying of cotton preparatory to nitration, care should be exercized that accumulations of dust in the drying apparatus be periodically removed.

3. In nitration, scrupulous care is to be observed that a drop of water does not fall into the centrifugal during or at the close of the acid removal process.

4. Efficient ventilation of the nitrating house, and danger from acid burns.

5. The nitrocotton immediately after removal of acid should be plunged into a large bulk of cold water and *thoroughly* disintegrated by stirring to guard against local decomposition. This precaution is unnecessary in the displacement method of nitration. The warmer the nitrated mass and the less the volume of water the more liable is decomposition to occur. Hence on warm, damp days, the nitrating centrifugals are more prone to *fume off.*

6. In the manufacture of guncotton blocks and cartridges, the pulped mass from the dehydrating centrifugal should be sifted in order to detect nails or other foreign matter, which

should be completely removed before the pressure is applied.

7. In guncotton compression, while in general the pistons perfectly fit the mold, yet there is no known metal which will indefinitely withstand the constant friction from pressure, and after a time will become wider in that part where the maximum compression has taken place. If the position of the molds and pistons are not precisely the same, then binding occurs, i. e., the mould will stand obliquely in respect to the piston, and a dangerous friction may result.

8. Where for certain purposes as in the manufacture of torpedoes, engineers cartridges, etc., the guncotton has to be turned in a lathe, drilled or planed, this should always be done under a constant stream of water, in order to keep the guncotton and the tool cooled.

9. During guncotton compression, ample protection should be given the men operating the valves.

10. In the drying operation, automatic electric appliances should be installed to indicate and warn against a rise in temperature above the considered permissible maximum.

11. Where the drying is assisted by means of a current of warm air passing over the nitrocotton, great care should be given to the proper grounding of the drying apparatus.

The use of ammonia for neutralizing the acidity in stabilizing nitrocotton, with the formation of ammonium nitrate, has long since been shown to be a real source of danger, and its use has been abandoned.

Transportation of Nitrocellulose (not explosives in general). Due primarily to a number of serious accidents in various countries, Austria,[1] Holland,[2] New Zealand,[3] United States,[4]

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[1] Transportation of Collodion in Austria, Phot. Corresp. 1877, **14,** 254.

[2] Industry and regulations of explosives in Holland, C. van-Pittius, Zts. Schiess. Spreng. 1908, **3,** 137.

[3] Importation, storage and transportation of explosives in New Zealand, The New Zealand Gazette, abst. Zts. Schiess. Spreng. 1908, **3,** 138.

[4] Regulations for transportation of explosives and other dangerous articles by freight and express, and specifications for shipping containers: Interstate Commerce Commission, July 2, 1914; abst. C. A. 1914, **8,** 3121. R. Adamson, Chapt. 10, Code of Ordinances, City of New York, 1915; abst. C. A. 1918, **12,** 426. Safety standard of the industrial board for plant manufacturing or using explosives, Pennsylvania, April 1, 1917; abst. C. A. 1917, **11,** 1547. Promotion of safety in transportation of explosives, etc., in the U. S. A.: B. Dunn, J. Frankl. Inst. 1910, **169,** 165; Bur. Explo. Reports,

England,[1] Germany[2] and other countries have either independently enacted laws or provided safeguards for the transportation of dangerous, inflammable and combustible materials. Of these materials, this topic has to do solely with nitrated cellulose.

Many, of the regulations in force in the various countries have apparently not been drawn with the assistance of experts in the subject of nitrocellulose, with the result that the regulations often work hardships on the guncotton manufacturers, being inconsistent in many important respects. This is an important matter, and has worked much hardship in the trade in the past, and proven a potent factor in deterring the development of manufacturing and distribution.

The Senate and General Assembly of the State of New Jersey have legally defined an explosive as "any chemical compound or any mechanical mixture that contains any oxidizing and combustible units, or other ingredients in such proportions, quantities or packing, that an ignition by fire, friction, concussion, percussion or by detonator, or any part of compound or mixture may cause such a sudden generation of highly heated gases that the resultant gaseous pressures are capable of producing destructive effects to contiguous objects, or of destroying life or limb, but not including colloided nitrocellulose in sheets or rods, or grains not under one-eighth of an inch in diameter, or wet nitrocellulose containing 20% or more of moisture."

While the various Governments have established rules which vary somewhat among themselves, yet one is typical of the others,

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see C. A. 1908, **2**, 1886; 1909, **3**, 838, 1085, 1592; 1910, **4**, 1809; 1911, **5**, 2178; 1912, **6**, 426, 1367; 1913, **7**, 2117; 1915, **9**, 1392; 1916, **10**, 1271; 1917, **11**, 1547. Regulations for the transportation of explosives in the U. S. A.; Oil, Paint and Drug Rep., July 18, 1908; abst. J. S. C. I. 1908, **27**, 834, 918; see also J. S C. I. 1908, **27**, 714. C. Beistle, Shipping Containers, J. Ind Eng. Chem. 1919, **11**, 674; abst. C. A. 1919, **13**, 1018, 1765. For a discussion of the common law liability in case of explosion of chemicals see C. Sherlock, Chem. Met. Eng. 1919, **21**, 83; abst. C. A. 1919, **13**, 2129.

[1] Transportation of guncotton, Wilson and Prentice, Chem. News, 1868, **17**, 195; Mon. Sci. 1868, **10**, 640; Dingl. Poly. 1868, **189**, 78; Poly. Centr. 1868, **34**, 1277; Wag. Jahr. 1868, **14**, 357. See also Arms & Explo. 1896, **4**, 107, 124, 147.

[2] For transportation of collodion cotton on railroads, etc., see H. Vogel, Industriebl. 1878, 126; Chem. Ind. 1878, **1**, 120; Phot. Corresp. 1875, **12**, 157; 1878, **15**, 17, 21, 45, 69; 1880, **17**, 168 208. German Railway Regulations for Transportation of Explosives; Zts. Schiess. Spreng. 1909, **4**, 111; abst. C. A. 1909, **3**, 1928. See also Zts. Schiess. Spreng. 1908, **3**, 176. Tests and regulations of the German Railway Administration, Zts. Schiess. Spreng. 1909, **4**, 175.

and the regulations of U. S. Interstate Commerce Commission are cited herein as indicative. It is forbidden to transport by freight "nitrocellulose in a dry and uncompressed condition in quantity greater than 10 pounds net weight in one exterior package."

Inside packages containing not more than 1 pound each of dry uncompressed nitrocellulose, wrapped in strong paraffined paper or other suitable spark-proof material, will be accepted for shipment if securely packed in an outside package that complies with Specification No. 14 and is marked as prescribed in paragraph 1559. Outside packages must not contain more than 10 pounds of dry nitrocellulose.

(c) The gross weight of an outside package containing not exceeding 10 pounds net of dry nitrocellulose, not compressed, packed as prescribed in paragraph 1555, must not exceed 35 pounds. Compressed sticks or blocks of dry nitrocellulose (guncotton) wrapped in strong paraffined paper may be shipped in outside packages complying with Specification No. 14, with a gross weight not exceeding 75 pounds.

1647. Detonating fuses or blasting caps or electric blasting caps in any quantity must not be loaded in a car or stored with high explosives of any kind, wet fulminate of mercury, explosive projectiles, explosive torpedoes, explosive mines, explosive bombs, nor with wet nitrocellulose, wet nitrostarch, wet picric acid, wet trinitrotoluol, or wet tetranitroaniline, or wet tetranitromethylaniline.

Nitrocellulose wet with solvent is an "inflammable liquid flashing at 40° F. Must contain not less than 30% by weight of a solvent whose flash point is not lower than 40° F., and must be packed in glass bottles, or in a securely closed metal vessel that will stand the drop tests prescribed for metal barrels. Nitrocellulose or nitrostarch wet with 20% water is an inflammable solid, while dry nitrocellulose and dry nitrostarch are high explosives."

"Nitrocellulose, nitrostarch . . . . uniformly wet with not less than 20 lbs. water to 80 lbs. of dry material . . . . must be packed in wooden barrels or kegs complying with Spec. 10, or in wooden boxes complying with Spec. 17, and marked WET NITROCELLULOSE—20% water. The gross weight of any box or keg must not exceed 450 lbs."

"High explosives are all explosives more powerful than ordinary black powder, except smokeless powders and fulminates. Their distinguishing characteristic is their susceptibility to detonation by a blasting cap. Examples of high explosives are . . . dry nitrocellulose (guncotton) and dry nitrostarch."

The Prussian Regulations regarding wet nitrocellulose are[1] that when containing at least 50% by weight of water or alcohol is not to be regarded as an explosive, provided proper care is taken in packing to avoid drying out. Nitrocellulose in this condition cannot be detonated by means of a blow, shock, flame or the action of a strong detonator.

F. Chamberlin[2] has proposed to ship explosives as nitrocellulose under a hydrocarbon oil, while J. Bouchard-Praceiq[3] advocates protecting nitrocellulose and other explosives during transportation by surrounding them with carbonates and moss.

Recent Advancement. In the method of cotton nitration of V. Smew[4] a series of nitrating vats are carried on a circular table, which is rotated to bring the vats in succession first beneath measuring devices from which they receive their charge of acid and material to be nitrated, and then beneath immersion and agitating devices for depressing the material into the liquid. From this, the material is automatically tipped into centrifugals and nitrated in the usual manner. C. Claessen[5] gelatinizes nitrocellulose by heavy pressure with aromatic nitro-bodies, and produces smokeless powders[6] in which the length is so adjusted with respect to the diameter that pre-determined ballistic effects may be obtained by partial peripheral gelatinization.

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[1] Ministerialbl. Handel u. Gewerbe, Mar. 14, 1911; Zts. Schiess. Spreng. 1911, **6**, 159; abst. C. A. 1911, **5**; 2950.

[2] U. S. P. 896622, 1908; abst. J. S. C. I. 1908, **3**, 961; C. A. 1908, **2**, 3283; Chem. Ztg. Rep. 1908, **32**, 510; Zts. Schiess. Spreng 1909, **4**, 96.

[3] E. P. 10129, 1908; abst. C. A. 1909, **3**, 1929; J. S. C. I. 1908, **27**, 1223; Zts. Schiess. Spreng. 1909, **4**, 137.

[4] E. P. 148124, 148125, 1920. See also F. Barrett, New method of detecting woody impurities in cotton and cotton waste, J. S. C. I. 1920, **39**, 81-T; abst. Chem. Zentr. 1920, **91**, IV, 150; Chem. Tech. Übers. 1920, **44**, 219. E. Beckett, Determination of N in nitrocellulose by means of the nitrometer, J. C. S. 1920, **117**, 220; abst. Chem. Zentr. 1920, **91**, IV, 207.

[5] D. R. P. 298565, 1916; abst. Chem. Zentr. 1920, **91**, IV, 206; J. S. C. I. 1920, **39**, 676-A.

[6] D. R. P. 298566, 1915; abst. Chem. Zentr. 1920, **91**, IV, 206. For the strength and velocity of detonation of various military explosives, see W. Cope, J. Ind. Eng. Chem. 1920, **12**, 870.

According to W. Delpech[1] French B-powder is converted by the addition of 3% vaseline or petroleum oil into a powder with no muzzle-flash. The nitrocellulose composition of J. Kessler[2] comprizes a cellulose ester and an alkyl ester of an acyloxy derivative of a higher fatty acid. J. Jarvis[3] diminishes inflammability in nitrocellulose by adding cellulose acetate, chloral hydrate and cinchonine. Gillet & Sons[4] gives to vegetable fibers the character of wool and an increased affinity and absorbent capacity for dyestuffs, by precipitating thereon nitrated starch.

J. Small and C. Higgins[5] have contributed valuable data on the manufacturing technique of cellulose nitration. The coated nitrocellulose powder of R. Woodbridge[6] contains an adherent coating of black power. The Akt. Ges. Siegener Dynamit Fabrik[7] gelatinizes collodion by warm nitroglycerol. The details of nitrocellulose manufacture have also been reported upon by H. Schlatter,[8] and of mixed acids by A. Hough, W. Savage and D. Van Marle.[9] The rapid determination of nitrocellulose has engaged the attention of H. Mallinson,[10] and the brisance of nitrocellulose explosives has been recently investigated by H. Kast.[11]

E. Knecht and B. Bostock[12] have shown that when guncotton is heated with water in a sealed tube at 190°, it undergoes hydrolysis, the guncotton disappearing and a pale, straw-colored liquid being left. The rate of hydrolysis depends on the relative proportions of guncotton and water used. If the temperature is lowered by more than about 2°, the hydrolysis is extremely slow, and if it is raised 10°–15°, a considerable amount of charring takes place. The amount of gas disengaged by heating 0.5 gm. guncotton with 25 cc. water for one half hour at 190° is 99 cc. The gas consists of CO, CO_2 and nitrous oxide and nitrogen. Some HCN and NH_3 are found in solution. Of the 13.05% N originally present in the cellulose nitrate, 10.24% is found as nitrous oxide and nitrogen, 0.43% as HCN, 1.20% as NH_3, 0.12% as nitrate, and 0.27% undetermined.

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[1] Genie civil 1919, **39,** 332; abst Zts Schiess Spreng 1920, **15,** 93, C A. 1920, **14,** 2708. In this connection see also G Esselen, The Chemistry of Cellulose from the Colloidal Standpoint, Chem Met. Eng 1920, **23,** 861 W. Gibson and R. McCall, Viscosity of solutions of nitrocellulose in ether-alcohol, J. S. C I 1920, **39,** 172-T, abst J C S 1920, **118,** i, 535, Chem Tech. Übers. 1920, **44,** 236; C. A. 1920, **14,** 2986 O. Silberrad, (U S. P. 1349983, 1920 abst. J. S. C. I 1920, **39,** 676-A) produces a flameless powder containing 30.7% nitrocellulose, 44% nitroglycerol, 21 4% starch and 3.9% vaseline.

[2] U. S. P. 1357876, 1920

[3] U. S. P. 1354401, 1920.

[4] E. P. 144204, 1919. See also Explosives Trades, Ltd. E P Appl 24313, 1920; abst. J. S. C. I. 1920, **39,** 618-A

[5] Chem. Age (N. Y.) 1920, **28,** 211, abst. C. A. 1920, **14,** 2710

[6] U. S. P. 1354640, 1920.

[7] D. R. P. 298420, 1916, abst. J. S. C. I. 1920, **39,** 676-A.

[8] Chem. Met. Eng. 1920, **23,** 591, 704

[9] Chem. Met. Eng. 1920, **23,** 666.

[10] J. Ind. Eng. Chem. 1916, **8,** 401; abst. C. A. 1916, **10,** 2524, Chem Zentr. 1920, **91,** IV, 235.

[11] Zts. Schiess. Spreng 1920, **15,** 181.

[12] J. S. C. I. 1920, **39,** 163-T, abst. J C S 1920, **118,** i, 535.

When guncotton is dissolved in aqueous NaOH on a water-bath, it is found that 65% of the total nitrate nitrogen is reduced to nitrite in order to provide the oxygen for the organic oxidation products which result from the hydrolysis. The extent of this reduction is nothing like so great in the alkaline hydrolysis, as in the neutral aqueous hydrolysis.

R. Farmer[1] classifies the different froms of decomposition of nitric esters as follows (see p. 1700): *a*, Decomposition of the pure esters. *b*, Accelerated decomposition. *c*, Hydrolysis followed by internal oxidation either by acids (slow but autocatalytically accelerated) or by alkalis (relatively rapid). *d*, The hydrolytic decomposition passes through the following phases: (*i*) incipient ester hydrolysis; (*ii*) internal oxidation, possibly to an alcohol peroxide (although this is speculative); (*iii*) formation of an aldehyde; (*iv*) decomposition to HO acids. When the conditions are such that the alcohol is protected from oxidation, it is readily regenerated as such on hydrolysis, thus showing that the first stage in the decomposition is a true ester hydrolysis of the normal type. The hydrolysis is shown to resemble that of other esters in its general relationships between velocity and concentration of H and HO ions, and the bearing of this relationship on the stabilization of nitric esters is shown.

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[1] J. C. S 1920, **117**, 806; abst. C. A. 1920, **14**, 2783.

CHAPTER X.

NITRATION OF CELLULOSE.

The method of presentation of the subject of the Technology of Cellulose Esters in this volume up to this point has been to detail some facts first in respect to the raw materials cellulose (pp. 1–388), starch (pp. 389–484), and especially cotton (pp. 485–583), which, because that is the form of cellulose usually nitrated, the various operations to which it is subjected in preparation for esterification are described and illustrated (pp. 584–665). Thus Part I closes with the cellulose just ready for nitration. Part II takes up the acids of nitration, nitric (pp. 665–1005) and sulfuric (1006–1402), and mixed acids (1403–1518), and the calculation tables required in connection therewith (1519–1566). Part III opened with a statement of the historical development of the cellulose nitrates (1567–1681), their physical properties (1682–1802) and combinations (1803–1932), and having discussed the raw materials entering into the cellulose nitrates and their properties, this Chapter is concerned with the practical methods which have been proposed from time to time for the laboratory production and commercial manufacture of the various kinds or grades of nitrocellulose, together with their technical details.

Part I ended with cellulose ready for nitration; Part II closed with mixed acids suitable for esterification; this Chapter takes the cellulose and the mixed acids from this point and unites them according to the various processes of nitration which have been proposed.

Synopsis of This Chapter. Cellulose is nitrated commercially either by hand (pages 1934–1940) as in the methods of Abel (1940–1942) or by direct dipping (1943–1951) or centrifugally (1952–1977) or by displacement (1978–1993). The du Pont mechanical system (1994–2002) and other esterification methods have been employed (2003–2032). In the nitration of paper (2033–2050) and lignin (2050–2054) special methods are used. After the preliminary washing of the nitrated cellu-

lose (2059–2067) and the possible utilization of the wash water (2067–2069), the nitrocellulose may be bleached (2069–2071), given a preliminary acid boil (2071–2083), after which it is beaten to a pulp (2083–2098). Further stabilization and blending is then accomplished by poaching (2098–2102), blending (2107–2112) removing foreign impurities mechanically (2102–2107) screening (2112–2114), after which the water still present is removed by means of wringing (2114–2127) or by hydraulic pressure (2127–2139) usually with the aid of alcohol (2139–2140). The finished nitrated cellulose is then dried (2145–2159) and the yield obtained is determined (2159–2160).

The guncotton may be compressed (2160–2188), granulated (2246–2249) or colloided (2249–2254) for specific uses. As typical of nitration practice in Great Britain the methods employed at Gretna (2188–2246) are illustrative. The co-nitration of cellulose with other bodies (2254–2256) and the classes of nitrocellulose produced in the United States (2256–2258), together with the official specifications for nitrocotton as laid down by the United States (2258–2265) and Great Britain (2265–2271) complete this chapter, and the various steps in connection with the transformation of cotton into the finished nitrated ester, as detailed herein.

Nitration of Cellulose by Hand. These processes, variously termed the "hand," and "pot" methods, are the outgrowth of the process with its refinements first inaugurated by v. Lenk, partially perfected by F. Abel, and improved by various refinements as will appear from the steps in advancements mentioned herein.

It will be remembered that the improvements as made by v. Lenk and heretofore briefly touched upon in the historical development of the nitrocelluloses (see p. 1593) are as follows:

"1st. The cleansing and perfect desiccation of the cotton, as a preliminary to its immersion in the acids.

"2nd. The employment of the strongest acids attainable in commerce.

"3rd. The steeping of the cotton in a fresh, strong mixture of acids, after its first immersion and partial conversion into guncotton.

"4th. The continuance of the steeping for forty-eight hours.

"5th. The thorough purification of the guncotton so produced, from every trace of free acid. This is secured by its being washed in a stream of water for several weeks. Subsequently a weak solution of potash may be used, but this is not essential.

"The prolonged continuance of these processes appears at first sight superfluous, but it is really essential; for each cotton-fibre is a long narrow tube, often twisted and even doubled up, and the acid has first to penetrate into the very furthest depths of these tubes, and has afterwards to be soaked out of them. Hence the necessity of time. It seems to have been mainly from want of these precautions, that the guncotton experimented on by the French Commission, gave irregular and unsatisfactory results."

In several of the large pyroxylin factories in England and on the Continent, and in at least two manufacturies in the United States, nitration by hand is made of a special grade of cotton which produces a very superior pyroxylin adapted for lacquers and bronzing liquids. Whether due to intentional misrepresentation to cover "secret processes" or a deficiency of intimate knowledge of the several steps involved, a large number, if not the majority of the recipes and methods to be found in text-books and the technical literature for preparing a nitrocotton best suited to this class of work are either directly misleading in some essential step, or else the methods of manipulation described are vague and lacking in detail. Aside from the interest attached to the method about to be described from the fact that the ester so produced has for many years answered the requirements of an exacting trade as to clearness, elasticity and strength, the details represent the successive steps in a commercial process in which there have been no recent essential changes, and in which, therefore, the nitrocotton produced has stood the test of time as regards commercial acceptability.[1]

That grade of medium-fiber Southern cotton known as Memphis Star is an upland cotton, and its fibers are very soft, moist,

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[1] Of the many methods for the preparation of pyroxylin to be found in the literature, the very great differences from each other both in composition of acid and method of procedure, make it quite a hopeless task to one of but little experience to select a method which will produce a given result. The lack of explicit information as to the condition of the cotton, temperature of nitration, duration of the operation, how to overcome the exigencies that are apt to arise during the progress of the process, yields, nitrogen content and solubility in a given solvent, render a great number of published methods incomplete or of little value. Perhaps in no other series of industries are the factory details more carefully guarded than in the industrial preparation of cellulose nitrate compounds.

Memphis Star is used in the unbleached state, the cotton being twice scoured. The first treatment consists in steaming in a 3% (calculated on the weight of cotton) solution of sodium carbonate crystals (washing soda)[1] for six hours in zinc-lined wooden vats, with tightly fitting zinc-lined covers. At the end of this period the cotton is washed with water until the alkali has been practically removed, when the operation is repeated. This time the steam is kept on for ten hours, and the amount of sodium carbonate reduced to 2%. The final washing is continued until the cotton is neutral, the wash water being clarified by passing through large sponge or sand filters. Scoured in this manner, dried cotton seldom gives more than 0.28% ether extract. Although in appearance cotton prepared in this manner is not as white as when bleached, the treatment results in but little change of the cellulose molecule.

The nitration is conducted in 5 gal. stoneware pots with tightly fitting lids in the top of which has been bored a $^3/_{16}$ inch hole for the escape of any fumes, and which also serves to warn the workmen of the commencement of burning or "fuming" of a "batch." The cotton is dried at 105° until no further loss in weight occurs, a $2^1/_2$ Av. lb. charge placed in air-tight containers similar to milk cans with rubber gaskets, and kept in a room at 35°–40° until ready for use. The charge of 2.1 U. S. gal. of nitrating mixture at a temperature of 56° is run into each pot, the latter having previously been placed in a water bath consisting of a wooden vat with perforated bottom and heated by steam. The acid mixture consists of 85.1%-85.2% total acids, of which 56% is sulfuric acid, leaving 29.1%-29.2% nitric acid and 14.8%-14.9% water. The cotton in small portions is immersed in the acid by means of aluminium forks, the handles of which are rubber covered to better prevent slipping. The heat of

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and elastic, a light, creamy-white color. This color is partially lost during scouring and nitration. The staple is short and the twist inferior to other grades, the straight, ribbonlike filaments being quite numerous. The cotton is carded but not bleached or scoured. It contains considerable half and three-quarters ripe fiber, which is extremely thin and transparent, distributed throughout the bulk of the pattern.

[1] It has been repeatedly asserted that factory experience apparently shows that crystallized sodium carbonate (Na_2CO_3, $10H_2O$) exerts a less drastic action on the cotton filament than the anhydrous form (soda ash) of sodium carbonate. The author has wondered if the small amounts of hydroxide sometimes found in commercial soda ash could account for the above belief.

reaction from the immersion of the cotton causes the contents of the nitrating pots to rise about 8°-9° above the entering temperature of 56°. After thoroughly stirring the cotton into the acid, the false bottom of the water bath is raised until the pots are entirely out of the water, where they remain until the temperature has subsided to 56° again, which usually requires about an hour. During this first hour the cotton is stirred only enough to guard against local overheating.[1] At the end of six hours' immersion the nitration is considered complete. The contents of the crocks are dumped into a centrifugal, the acid extracted and the cotton "drowned" by plunging into a large volume of cold water in the usual manner. Neutralization is effected by boiling alone, and without the addition of alkali.[2] The nitrocotton is pulped, and dried on cloth screens, by means of a current of filtered dry air which enters so as to pass through the nitrocotton from the bottom upward. The ceiling and walls of the dry-house are plastered, the cement floor being covered with linoleum or rubber.[3]

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[1] Whenever red fumes are observed during the nitration process, the mass in the pots must be carefully but very thoroughly stirred. During the entire process the cotton must be stirred no more than absolutely necessary, for stirring disintegrates the fiber and causes loss in washing. One of the main points in favor of the Thomson displacement process is the fact that the cotton is not broken during nitration, and hence larger yields are obtained. If it is desired to make the cotton more fluid, the initial nitration temperature may be raised to 58° or 59°, and if this does not have the desired effect, instead of allowing the pots to cool to 56° in the air as in the original process, they may be placed in the water bath at once. It is the first temperature that governs most strongly the production of a fluid nitrocotton. From the action of the first batch in the nitration mixture subsequent batches can be modified. Three men nitrate 65 pots in one working day of ten hours. In nitrating, if it is found that the physical condition of the pyroxylin will stand it, the temperature of the water bath is raised from 55° up to as high as 65°, this rise tending to increase the fluidity and clearness of the pyroxylin when dissolved, but at the same time slightly decreasing the yield. Notwithstanding theory to the contrary, it is the observation of the nitrating workmen that on damp, heavy, foggy days, the nitric acid in the nitrating fluid decomposes more readily; the nitrocotton tenders more easily in the pots and requires more careful attention to preserve the yield. The value of sulfuric acid is not, as has often been assumed due merely to its power of combining with water formed during the reaction, but also perhaps to the formation of sulfuric acid esters, subsequently converted into nitric esters. The longer then, within reasonable limits, the cotton is left in contact with the acids, the more complete probably will be the conversion into nitric acid esters. The sulfuric esters according to this view, therefore, are merely transition bodies.

[2] In corroboration of the experience of others, it has been found that when alkali is omitted, the pyroxylin requires fewer washings for neutrality, and gives longer stability tests.

[3] To prevent vermin from entering the building, and the impalpable pyroxylin dust collecting in cracks.

The workmen wear sewed rawhide sandals. The temperature is automatically regulated between 30–35°. Usually three days are required for drying, the moisture being about 22% as the nitrocotton leaves the hydroextractor. The nitrogen per cent. is within the limits 12.65–12.75, usually nearer 12.65%.[1] The nitrocotton is above 98% soluble in ether-alcohol, above 96% soluble in a mixture of amyl acetate 60 (by volume) and benzine 62° Bé., 40, this latter solvent mixture being of much more importance in the lacquer industry than ether-alcohol, the latter solvent being seldom used. The viscosity[2] is governed in the nitrating pots largely by the following observations:

(1) If the first pot nitrated tenders too much, as indicated by the "feel" with the stirring rod, the viscosity will be too low, and subsequent batches are to be put in at a slightly lower temperature, perhaps 53°–54°.

(2) If the cotton falls to the bottom of the nitrating fluid, feels harsh, and but little chemical action is evident, the acid is probably deficient in nitric acid, and a higher temperature of immersion must be taken, or the nitrocotton will have a high viscosity and in the majority of cases a high insoluble residue in amyl acetate-benzine.

(3) If the cotton in the nitrating acid floats to the top (heaves) buoyed up by the nitric oxide fumes evolved, this indicates a slight excess of nitric acid. Such a batch must be watched closely and stirred at frequent intervals to prevent fuming.

(4) If the cotton in the nitrating bath feels soft ("mushy") the sulfuric acid is evidently in excess, and if the heat of reaction

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[1] At this particular works a large number of experiments have been undertaken to determine the reason why a pyroxylin solution once filtered will, or will not, deposit from 1%–6% solid matter (lower cellulose nitrates) upon standing in solution in daylight. Careful comparisons of nitration formula, viscosity, original solubility and percentages of nitrogen have not resulted in conclusive results. It is not a matter of room temperature and is a subject of considerable moment to manufacturers of lacquers, photographic films and artificial silks. Pyroxylin intended for artificial leather and the less expensive bronzing fluids is never dried, but hydroextracted either in centrifugals or hydraulic presses, and the remainder of the moisture removed by displacement with a pyroxylin non-solvent as denatured ethyl alcohol or the lower fractions of fusel oil

[2] A desired viscosity is obtained by blending pyroxylins of a viscosity higher and lower than that required. The "viscosity factor" is an arbitrary number used, and obtained by taking the grams of pyroxylin per hundred cc. in a given solvent combination and multiplying by the time required to pass through the orifice of the viscosimeter.

does not give the normal rise,[1] the yield will be poor, and probably contain much insoluble matter.

While the length of time is stated as six hours' immersion, climatic conditions and the humidity of the atmosphere apparently make a difference in the nitration time, and irrespective of the length of immersion the batches are considered finished when they have a certain softness or "feel" to the workmen when the batch is stirred with a fork. Large yields are not sought, but rather fluidity and solubility of the nitrocotton is the first consideration. Something in the way of yield must be sacrificed in order to obtain high fluidity, because the higher temperatures required to obtain a desired viscosity always cause an appreciable loss of nitrated cotton, not only from passing into solution in the reacting mixture, but also in the subsequent washings, especially after having been pulped.

The dried product is tested for its suitability for certain classes of lacquers and bronzing fluids, by dissolving 1 gm. in 60 cc. amyl acetate and 40 cc. benzine.[2] The following observations of the solution so formed have been found generally true for the specific nitrating formula given above.[3]

If the solution in amyl acetate-benzine is:

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[1] It requires ordinarily about fifteen minutes to attain the maximum rise, and an additional thirty minutes for the temperature to return to that of the nitrating acid before cotton immersion.

[2] The pyroxylin is first moistened with 30 cc. amyl acetate and after having been stirred until homogeneous, is diluted with the balance of the solvent, previously mixed. In this manner much more rapid solution is effected than by the addition of 100 cc. of the above mixture at one time; benzine, it will be remembered, is a non-solvent of any form of cellulose nitrate, being used only because it is the cheapest commercial anhydrous fluid. Cellulose nitrates may be more soluble in amyl acetate than in the above mixed solvent, but the latter is used because it approximates the formulas used in manufacture. A pyroxylin which entirely dissolves in both amyl acetate and amyl acetate-benzine 60 to 40, will have an appreciably higher viscosity in the latter solvent mixture.

[3] These generalizations are mean results obtained from testing each day's product for solubility during many months, and in connection with the daily reports from the nitrating house as to the deportment of the cotton in the nitrating acid. Where the nitric oxides are in excess in the nitrating mixture, a higher rise in temperature than usual occurs when the cotton is first immersed; incipient decomposition of the nitric acid is more liable to occur (i. e., the spent acid is unusually weak); the temperature falls more quickly after the maximum has been reached; the time of immersion is decreased; and more attention by the workmen is required to prevent fuming and to preserve the normal yield.

It seems to be a fact that the whitest and clearest nitrocotton is obtainable by pot nitration in earthenware pans, and that centrifugal nitration

(1) Thin and turbid, the temperature of the nitrating acids was too low, that is, there was too much water present during nitration.

(2) Heavy and turbid, the temperature of the nitrating acids was too low at the time of immersion, or the cotton was not thoroughly stirred therein, probably the former.

(3) Thin and clear, yield about 140%-144% (calculated on the weight of the cotton as dried at 105°); all nitrating factors right.

(4) Heavy and clear. Nitric acid high, sulfuric acid low; temperature low, nitration process fully six hours, cotton floated to top of batch during nitration period and required careful attention.

It is evident that a certain amount of skill and cleverness embraced in the word "experience" is necessary for the success of any technical process, and especially in a process of nitration which introduces several variables. But it is not too much to state that careful attention to the details as above enumerated in the hands of a person of moderate experience will enable that person to continually produce a nitrocotton especially adapted to the preparation of modern pyroxylin lacquers.

Abel Method of Nitration. The method of cotton nitration as described before the British Association in 1863 by F. Abel as an improvement upon the Lenk system, is a two stage nitration, and was the one universally employed in principle until comparatively recent times, and even to-day, like the hand nitration process previously described, isused in the production of pyroxylin

does not give as satisfactory pyroxylins in this respect. Undoubtedly the absence of iron, and the fact that in the pot method the nitration is under greater control, and hence can be more quickly modified to meet existing emergencies that occur in the nitrating bath, as variations in temperature, but especially the "feel" of the cotton during the nitration process. For the manufacture of so-called "collodion cotton," and in general the lower nitrogen content nitrocottons, weaker total acid mixtures are employed than for guncotton manufacture. Equal parts of 75% monohydrate nitric acid and 96% monohydrate sulfuric acid, at 1 to 1½ hours at 40°-50° is a formula used for some years by a large manufacturer in the United States. The above formula is varied somewhat depending on the weather conditions, as is well known to those engaged in nitration. In any case, the degree of nitration is shown to be a function of the water content of the acid mixture and the temperature of the same. Whereas concentrated sulfuric acid changes cellulose to sugar on warming, and concentrated nitric acid changes cellulose to oxalic acid, both acids mixed produce neither oxalic acid or sugars in notable amounts, but esterification results.

for special purposes, especially for lacquers and collodions.

In the first portion of the process, the cotton is dipped in a large bulk of nitrating acid for a few minutes and is then squeezed from excess of acid and placed in a small pot where it is left for several hours for the second part of the nitrating operation. It should be borne in mind that the composition of the acid mixture in the dipping pans is *not* the same as that added after dipping, the former being of much higher nitric acid content.

The detailed description of the Abel process, as formerly carried out in England at Waltham Abbey, is given by F. Nathan[1] as follows:

"The nitrating acid was composed of three parts of sulfuric acid of 96% mono-hydrate to one part of nitric acid of 91% mono-hydrate, thoroughly mixed and cooled. This acid was run from the store tanks into cast iron dipping pans, holding about 220 lbs. each, the pans being supported in an iron tank through which cold water circulated, to keep the temperature below 70° F. The dipping pans were provided at the back with gratings, on which to press out some of the acid from the charge. The charge of cotton waste weighed 1 lb. 4 oz., and on removal from the cooling box was passed from the back through an earthenware pipe in the partition running along the back of the pans, and raked by a dipper, as rapidly as possible, into the acid. After remaining in the acid bath for about eight minutes, the cotton was removed to the grating and a portion of the acid squeezed out by means of an iron lever having an iron plate attached to one end. After a charge had been removed from the dipping pan about $13^{3}/_{4}$ lbs. of the mixed acid was run into it to replace the amount removed with the charge. The charge, now weighing with the adhering acid about 15 lb., was placed in an earthenware pot provided with a cover and transferred to the cooling pits, through which a stream of cold water flowed, and where it remained for 12 hours. During this period of digestion the conversion of the cotton into guncotton was completed.

"The contents of the pots were now emptied into a centrifugal wringing machine, and the bulk of the waste acid extracted. The guncotton was then removed from the centrifugal machine and placed in galvanized iron pans with long handles. These pans, when filled, were carried quickly across to the immersing tank and the guncotton thrown into a large bulk of water, the workmen standing by the tank and pushing the guncotton at once under the water with a stout wooden paddle. The immersing had to be done as quickly as possible, as, if the guncotton were allowed to come gradually in contact with water, it was liable to fume off. The immersing tank was fitted with a perforated copper plate, to allow the water to overflow, so that fresh water was constantly passing through the tank. The guncotton was kept well stirred by means of a wooden paddle. When 2 cwt. had been immersed, the inflow of water was stopped and the tank drained down. When all the water had been run off the tank was filled up again with fresh water. This was repeated six times or until the guncotton no longer tasted acid. When this stage had been reached the guncotton was wrung in a centrifugal machine, water from a hosepipe being turned on the guncotton for one minute during the wringing, and it was then ready for boiling.

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[1] J. S. C. I. 1909, **28**, 177, 181; abst. C. A. 1909, **3**, 1342; Chem. News, 1909, **99**, 83; Bull. Soc. Chim. 1910, **8**, 60; Mon. Sci. 1910, **72**, 111; Rep. Chim. 1909, **9**, 376; Chem. Zentr. 1909, **80**, I, 1678; Chem. Ztg. 1909, **33**, 208; Chem. Ztg. Rep. 1909, **33**, 146; Jahr. Chem. 1909, **62**, II, 388; Meyer Jahr. Chem. 1909, **19**, 333; Wag. Jahr. 1909, **55**, I, 431; Zts. ang. Chem. 1909, **22**, 1614; Zts. Schiess. Spreng. 1909, **4**, 285, 327

"This process, although it undoubtedly produced a good guncotton, had certain disadvantages, and the amount of labor required was very great. The plant, although individual items were not expensive, very rapidly deteriorated, and the cost of renewals and replacements was heavy. Power was required to drive the centrifugal machines, large quantities of water were used both for cooling and immersing, and decompositions, both in the pans, pots, and acid centrifugals, were by no means an infrequent occurrence."

The method of pot nitration as carried out in England is shown in Figs. 146 to 149, and in France, in Fig. 145.

The "tank" method of nitration is a development of the "pot" method, the weight of cellulose used in one operation, and the ratio of acids to cellulose being increased. The ratio of acids to cellulose varies from 1:25 to 1:50, depending upon the properties of the resulting pyroxylin desired. The cellulose is allowed to remain in the acid mixture for variable periods, depending upon the viscosity and solubility required of the finished cellulose ester.

The nitrocellulose may be raked out from the acids and placed in a centrifugal, or the contents of an entire tank may be emptied into a wringer and the acids extracted. The recovered acids are fortified by the addition of fresh acids, and re-used several times.

Direct Dipping Method of Cellulose Nitration. It will be recalled that in v. Lenk's system of guncotton manufacture the operation of nitration was carried out in two stages. The first stage was the dipping of the cotton in mixed acid contained in nitrating pots or pans, while in the second, the nitration was completed by allowing the partially or incompletely nitrated cotton to remain in contact with a weaker acid in earthenware pots for a prolonged time, sometimes as long as two days. The loss of nitrated cotton by occasional decompositions in the digesting pots, and the labor entailed in handling them undoubtedly were disadvantages, and led some manufacturers to revert to the even older method of esterifying in one stage. In this system, which has been called the "direct dipping" method, the size of the individual nitrating pans was reduced to enable them to be lifted on to trucks by hand, wheeled to the acid centrifugals and

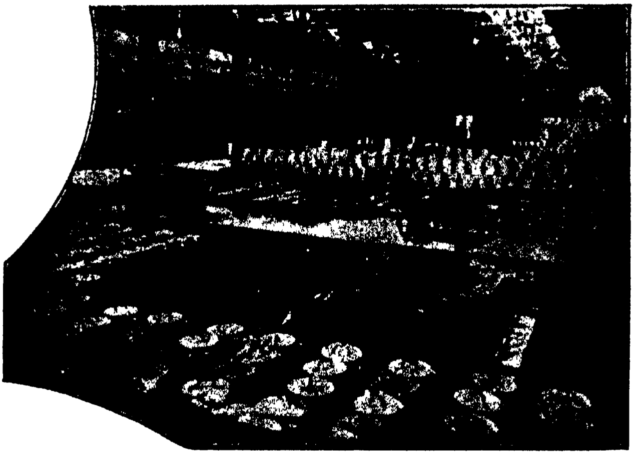

FIG. 145.—POT NITRATION OF CELLULOSE IN FRANCE

their contents emptied into them, thus economizing time.

This direct dipping process was probably the first attempt which was attended by any considerable degree of commercial success to overcome some of the inherent disadvantages of the Abel process. This method as used on a large scale at Nobel's factory at Ardeer, Scotland, is given by F. Nathan[1] as follows:

"The installation consists of parallel double rows of long iron tanks known as "coolers." Iron pots termed "dippers" in which nitration is carried out stand in the coolers, 62 to each cooler. Sliding wooden covers rest on the coolers to guide the fumes from the dippers into earthenware pipes with openings at intervals, through which they are drawn by exhaust fans. The mixed acid, either cooled or warmed as necessary, is carried by lead pipes placed between each row of coolers, and is supplied to the dippers through earthenware cocks at intervals.

"*Nitration.* The water in the coolers is kept at 15°. The dippers, having been placed in position in the coolers, are each filled with 127 lbs. of mixed acid by measurement, from the acid taps. $4^1/_2$ lb. of cotton waste are steeped in each dipper. To minimize decompositions each charge of cotton waste is added in about ten installments. The wooden covers are only removed to allow steeping to be done, and are then at once replaced. The temperatures of nitration are: Initial temperature of mixed acid, 15°; maximum after steeping, 25°; temperature at end of nitration, 20°. The duration of the nitration varies according to the output required from the plant. One, two, or three shifts may be worked per twenty-four hours, and the time of nitration may, therefore, be twenty-four, twelve, or eight hours respectively.

"The average composition of the mixed acid for a twelve hours' immersion is as follows: Sulfuric acid, 75.0%; nitric acid, 15.75%; nitrous acid, 1.30%; water, 7.95%. For an eight hours' immersion a higher percentage of nitric acid and less water is used; for a twenty-four hours' immersion less nitric and more water. The average composition of the waste acid for a twelve

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[1] J. S. C. I. 1909, **28,** 177, 181; abst. C. A. 1909, **3,** 1342; Chem. News, 1909, **99,** 83; Bull. Soc. Chim. 1910, **8,** 60; Mon. Sci. 1910, **72,** 111; Rep. Chim. 1909, **9,** 376; Chem. Zentr. 1909, **80,** I, 1678; Chem. Ztg. 1909, **33,** 208; Chem. Ztg. Rep. 1909, **33,** 146; Jahr. Chem. 1909, **62,** II, 388; Meyer Jahr. Chem. 1909, **19,** 333; Wag. Jahr. 1909, **55,** I, 431; Zts. ang. Chem. 1909, **22,** 1614; Zts. Schiess. Spreng. 1909, **4,** 285, 327.

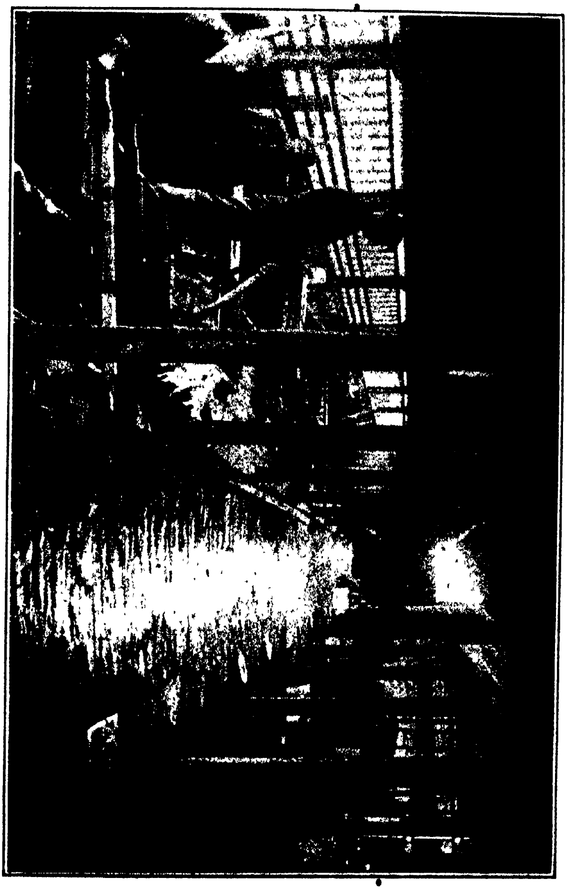

FIG. 148.—THE DIRECT DIPPING OF CELLULOSE

hours' immersion is: Sulfuric acid, 77.8%; nitric acid, 11.0%; nitrous acid, 1.5%; water, 9.7%.

"*Recovering the Waste Acid.* When the nitration is complete, the "dippers," covered with light aluminium lids, are placed on barrows, wheeled to the centrifugals, situated at the end of the "coolers," and the whole contents tilted out into the centrifugal. Four dippers are loaded into each centrifugal, and the guncotton having been uniformly spread round the basket, the centrifugal is run for six minutes, to remove waste acid. At the end of that time about 1 lb. of waste acid is still adhering to each pound of guncotton. The centrifugal cover, made of light aluminium, is not fixed to the centrifugal in any way, so that as little resistance as possible may be offered when there is a decomposition. This is the usual arrangement in the case of acid centrifugals. The cone of the centrifugal projects through a circular opening in the center of the lid and is covered by a small loose aluminium box. Small holes are cut in the sides of this box, and are of service in warning the workmen when there is a decomposition, as fumes are generally seen to issue there first.

"*Drowning the Guncotton.* When the waste acid has been removed the guncotton is quickly lifted out of the centrifugals and thrown under the revolving paddles of the drowning tanks, which immediately immerse it. The men who do the discharging are provided with rubber gloves and wear thick flannel hoods, which completely cover the head, arms, and breast. The hoods are fitted with strong glass windows, and are connected by light rubber tubing to a supply of pure compressed air.

"*Prewashing.* After a given quantity of guncotton has been drowned, the water in the tanks is run off and the guncotton thrown onto draining tables forming part of the drowning tank. It is then loaded into the prewashing centrifugals, the acid water wrung out, and washed for a few minutes with cold water from a hose, to remove adhering acid. No special precautions, however, are taken to remove all acid at this stage. The bulk of the water having been removed, the guncotton is loaded from the centrifugals into bogies, and conveyed to the boiling house.

"The 62 dippers in each cooler form a "charge." Eight charges are worked by each shift. The yield is 159% of dry guncotton on the dry carded cotton. The output per shift consisting of

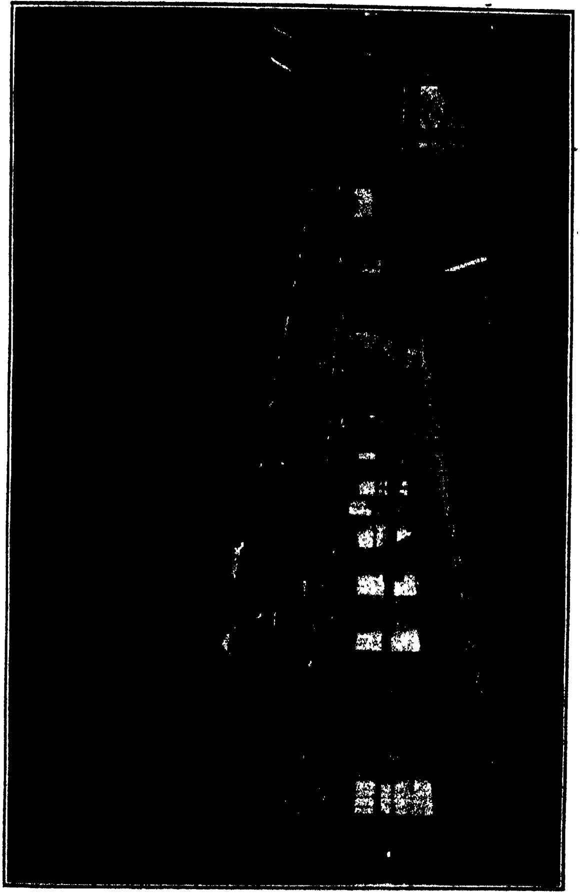

FIG. 149.—NOBEL'S EXPLOSIVES COMPANY'S TANK METHOD OF NITRATION

seventeen men is, therefore: 4.5 × 159 × 62 × 8 ÷ 100 = 3549 lbs."

In Germany, the method of direct dipping-nitration carried out is, in general, as follows: A separate storage vessel for nitric and for sulfuric acids is provided, which are mixed in the desired proportions shortly before use. The individual nitrating pots are immersed in a trough of warm water, the nitrating pots standing upon a removable structure. Each pot is provided with a false sieve bottom, two outlets, a two-piece lid, one piece being removable, through the front half of which passes a curved pipe. The outlets have a stopcock, and end in a common line leading to a trough for the waste acid. A stage is provided in front of the pots, over which is a water pipe line with faucets and hose.

The curved pipes are connected with a pipe leading to a tower for the absorption of fumes. The nitration process is conducted as follows:

The nitrating mixture warmed to the desired temperature, is filled in the pots to a certain mark, a weighed amount of cotton in flocks placed in the pots with stirring, care being exercized that each addition of cotton is thoroughly wetted by acid before the next portion of cotton is immersed. When all the pots have been thus filled, the material is thoroughly stirred, the outlet cock opened and the nitrating acid allowed to run out. The outlet cock is then closed, and the pots submerged in the warm water. After steeping for a stated time, the nitrated cotton is drowned by means of cold water from the water line above, the vapor evolved in the operation being conducted to the tower, where it is condensed by means of water and discarded. The cotton is then withdrawn from the pots, and the latter prepared for a further nitration.

In the method of S. Assadas[1] two of a series of stoneware pots are charged with pure paper cellulose contained in a "basket" of acid-resisting material. A charge of mixed nitric and sulfuric acids is then run into one pot and nitration proceeds with exclusion of light and air, at the temperature of the water bath in which the pots are immersed. This pot is then raised by a pulley and connected by means of a pipe with a funnel in the lid of the other;

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[1] E. P. 9982, 1908; abst. J. S. C. I. 1909, **28**, 671; C. A. 1910, **4**, 107; F. P. 387537; abst. C. A. 1909, **3**, 1819; J. S. C. I. 1909, **28**, 873; Mon. Sci. 1909, **71**, 14.

the spent acid being tapped off into the second pot, into which a charge of fresh acid is run through a funnel. The two pots are then disconnected. The nitrocellulose from the first pot is then emptied into cold water, a fresh charge of cellulose put in, and the nitrating operation repeated, the pots being reversed. The apparatus is shown in Fig. 150.

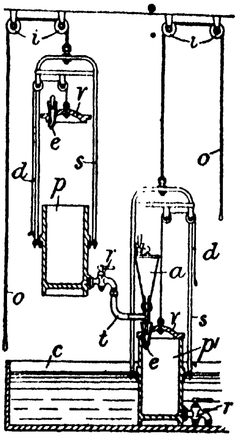

Fig. 150.—The Assadas Method of Cellulose Nitration

According to the Patronenfabrik Saxonia,[1] amorphous nitroproducts of oxy- and hydrocelluloses are prepared by treating cellulose with a mixture of sulfuric acid and a small quantity of nitric acid, with cooling, until the mass begins to become pasty, then adding the required quantity of concentrated nitric acid to effect the nitration, and deacidifying and washing the product in the usual manner. For example, 100 gm. of paper-cellulose are introduced into a mixture of 500 gm. of 85.5% sulfuric acid with 3.5%–4% of concentrated nitric acid, to which 2%–2.5% of water has been added. The cellulose is kneaded with the acid mixture, the temperature being kept at 2°–3°, and 100–120 gm. of nitric acid of 48° Bé. are then added. The nitration is complete in about 15 minutes.

In the W. Wunderlich apparatus,[2] the base of the nitrating vessel has a false superposed bottom, the first portion being indented or hollowed out. The second portion is similar in shape, but larger and flatter. In the first part, stirrers are so mounted that twice in each revolution they plunge beneath the nitrating mixture, carrying along any material to be nitrated, pushing it over the raised portion into a second trough or depression. The acid is at the same time propelled toward a perforated drum, against which a solid roller presses. The wringer arrangement siezes the nitrated material and squeezes out the acids, the nitrated cellulose being removed from the perforated drum by means of a scraper. The arrangement is so made that the acids circulate in a pre-determined direction.

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[1] D. R. P. 198284, 1903; abst. J. S. C. I. 1908, **27**, 837; Zts. ang. Chem. 1908, **21**, 1661; Chem. Zentr. 1908, **79**, I, 1912; Jahr. Chem. 1905–08, II, 973; Chem. Ztg. Rep. 1908, **32**, 283; Chem. Ind. 1908, **31**, 352; Wag. Jahr. 1908, **54**, I, 430; Zts. Schiess. Spreng. 1908, **3**, 214; Mon. Sci. 1911, **75**, 93.

[2] D. R. P. 65399, abst. Ber. 1893, **26**, 124; Wag. Jahr. 1893, **39**, 427 Zts ang. Chem. 1893, **6**, 21; Mon. Sci. 1893, **42**, 861.

Weiss[1] seeks to remedy over nitration by the addition of dilute ammonium hydroxide solution to the nitrated cellulose alleging that a nitrocotton insoluble in alcohol-ether can be reduced in nitrogen content by this treatment until a complete solubility results. The nitration methods of F. Hardwich,[2] and of A. Sharp[3] are of but historical interest.

The Centrifuge in Cellulose Nitration. The centrifuge today has attained a widespread use in nearly all branches of the explosive industries, the chief use, however, being in the nitration of cotton. In the esterification of cotton, centrifuges are used in nearly all stages of the process from the preliminary nitration to the final washings and sometimes to the point of dehydrating prior to colloiding. In the preparation of nitroglycerol explosives however the use of the centrifuge has not been attended with success where attempts were made by A. Nobel,[4] to remove the excess of nitroglycerol by means of centrifugal force in the manufacture of Ballistite. This dangerous operation however was soon supplanted by the more practical processes of Lundholm and Sayers.

Although the manufacture of nitrated hydrocarbons also extensively employs the centrifugal, as for the separation of mother liquors in crystallizing operations; and in the removal of wash water and alcohol as exemplified in the production of picric acid and trinitrotoluol. These uses are outside the topics treated herein. The various centrifuge systems and apparatus may be classified in the technology of cellulose esters into the following five subdivisions, all but number four being used in nitration.

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[1] Pharm. Ztg. 1891, 113; abst. Proc. Amer. Pharm. Assoc. 1891, **39**, 587; Chem. Centr. 1891, **62**, I, 681; Wag. Jahr. 1891, **37**, 749; Jahr. Pharm. 1891, **51**, 351.

[2] Brit. J. Phot. 1901, **48**, 643; abst. J. S. C. I. 1901, **20**, 1239.

[3] Maryland J. Pharm. 1858; abst. Proc. Amer. Pharm. Assoc. 1859, **8**, 79.

[4] D. R. P. 51471; abst. Jahr. Chem. 1890, **43**, 2708; Chem Ztg. 1890, **14**, 670; 1892, **16**, 1278; Chem. Tech. Rep. 1890, **29**, I, 223; Chem. Ind. 1890, **13**, 167; Wag Jahr. 1890, **36**, 541; Ber. 1892, **23**, 528; Mon. Sci. 1891, **37**, 426; 1905, **62**, 87; Meyer Jahr. Chem. 1891, **1**, 333; Tech. Chem. Jahr. 1889, **12**, 168; 1892, **15**, 175.

1. With cold or hot water (hydro-extractors).
2. With steam or air (steaming or exhausting centrifuges).
3. With nitrating acids (nitrating wringers).
4. With mother liquors.
5. With alcohol (solvent dehydrating or alcoholizing centrifugals).

As the result of these diversified uses the manufacturers of this class of machinery have for some time and are at present actively engaged in the development of various types especially suited to the use to which they are intended to be put. The extraordinary demands for strength, stability and durability made on centrifuges, especially when they are designed to operate at high speed or in intensive use, make the selection of suitable materials and accurate machining imperative.

The various regulations for the construction and operation of centrifuges as formulated by the trade unions of the workers engaged in the industries using them, stipulate primarily that the machine shall be equipped with such a drive that the operation, or rotation of the same, can only be performed after the covers or safety guards have been closed; also that a reliable tachometer with an alarm bell or similar device be installed so as to enable the operator to know at all times the speed of rotation of the apparatus and thus prevent accidents. The construction of the various safety devices differs widely. In some cases, for instance, the removal of the cover is only possible when the driving belt has been pushed over on the loose pulley; and conversely that the drive can only be put on after the cover has been closed. This, of course, does not prevent the opening of the centrifuge while it is still spinning from its momentum while the centrifuge is operated by direct steam reciprocating or turbine drive, or direct coupled electric motor; in such cases the cover can be so mounted as to automatically shut off the steam or current whenever the latter is lifted. Of the many forms of safety devices which have been brought forward, there is one which is independent of the form of drive, being dependent only on the number of revolutions of the centrifuge itself, so that the cover can only be opened when the revolutions do not exceed a certain number per minute. One of the devices as brought out by Gebrüder Heine, makes use of the air which is circulating in the space between the rotating drum and the walls of the machine, a pendulum being suspended in this space, so arranged that the pressure of the air when the drum is in motion will displace it from the vertical and thus actuate a hook which holds down the cover. When the centrifuge stops, the pendulum will swing back into the vertical position and permit of opening the cover. The latter in turn is connected with a belt or gear shift, or, in the case of steam or electric driven centrifuges with the valve or controlling levers as the case may be. This type of safety device can, however, be used to advantage only in the absence of corrosive liquids, or, where the amount of liquids thrown off into the space between the shell and the basket is too great, as for instance with nitrating centrifuges. For such cases a similar device actuated by a belt from the main drive has been developed. In this mechanism the centrifuge cover is firmly connected with the spindle and two levers which are movable in their bearings. One of the levers is connected with a pushing rod while the other lever is connected to a similar rod with a locking bar. A bell shaped receptacle is mounted so as to rotate on a spindle and this contains a pendulum. As soon as the belt begins to move, the receptacle will commence to rotate, thus displacing the pendulum from the vertical and bringing its upper part directly under a rod which prevents the latter from moving downward. This in turn prevents the opening of the cover until the centrifuge or belt stops, when the pendulum returns to the vertical allowing the rod to move downward and thus releasing the cover. If desired, this arrangement may be fitted to a steam or an electric driven machine, by slight modifications.

There has recently been issued to the firm of C. Haubold, a patent for a simple and apparently effective mechanism for this purpose. This device is not in contact with any of the liquid or solid ingredients of the centrifuge, is not subject to friction, and in no way interferes with the strength and operation of the machine. It consists essentially of a double iron lever, mounted so as to be horizontally movable, in a closed box attached to the shell of the centrifuge. A hook protruding from the top of this box engages the bolt which holds down the cover. To retain the hook in position when the machine is in motion, a current of air, derived from a small ventilator attached to the drive of the centrifuge, is passed through a tube to the box thus preventing the disengagement of the hook until the speed has decreased to a certain predetermined point. In this way the safety device is independent of the method of driving, as it is actuated by the rotation only. An improved belt shift is provided which necessitates closing the cover before the belt is thrown on.

Brakes are of paramount importance and should be arranged so that they can be used only after the belt or power has first been thrown off, automatic brakes being preferable because they operate as soon as the power has been discontinued. Sparks, of course, must be prevented on account of the fire hazard involved. Over-driven centrifuges to-day have been almost entirely displaced by under-driven machines on account of the danger of flying belting, or grease and oil, from coming in contact with the nitrated material. In the installation of centrifuges, unusually good foundations are required as well as careful machining of the bearings and adequate strength of materials to withstand the centrifugal force.

Centrifugal Nitration of Cellulose. This method may be regarded as the tank process in which the tank consists of a centrifugal. In order to minimize the laborious and unpleasant operations of transporting nitration pots and contents from the dipping pans to the cooling pits, and at the close of the nitration process, carrying the pots to the acid centrifugals, and the several transfers of acid and cotton from one vessel to another, a method was first commercially developed in Germany and since has been widely applied, whereby the nitration and acid elimination takes place in the same vessel, i. e., a centrifuge.

In 1890 H. de Chardonnet[1] patented a process for placing the nitrated cotton in a centrifugal in order to recover the maximum of spent acids, this being the first definite application of the centrifuge to the nitration of cellulose. In this method the cellulose was nitrated in the ordinary manner, the nitrocotton and mixture of acids being then transferred to a centrifugal, "by which means about three-fourths of the acids are recovered and may be used after being strengthened by addition of fresh acids."

R. Kron[2] made some minor improvements in the centrifugal machine in the way of providing a perforated basket adapted to be tipped, in combination with a surrounding cylinder or guard which could be raised clear of the basket while the latter was being tipped, but apparently neither commercialized their ideas beyond obtaining patent protection.

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[1] E. P. 5376, 1890; abst. J. S. C. I. 1891, **10**, 566.

[2] E. P. 13612, 1891; abst. J. S. C. I. 1891, **10**, 740, 746, 872, 880,

Selwig & Lange Nitrating Centrifugals. It apparently remained for J. Selwig and B. Lange, constituting the firm of Selwig & Lange, to combine in 1891, the nitrating of the cotton and squeezing of the spent acid in one and the same receptacle, a centrifuge. Their original apparatus shown in Fig. 151, comprizes the basket *A*, arranged to be rotated by the shaft *b* from the pulley *c*. It is first filled with cellulose, and then nitrating acids are admitted through a pipe to the cylinder *B*. During the nitration the temperature is regulated by liquid passing into the jacket *h*. After the nitration has been completed, the spent acids are withdrawn through the cock *C*, after which the basket is rotated to drive out the remaining acid from the nitrocellulose, which is then immediately taken out and immersed in a large volume of running water.[1]

In 1899, L. Morane[2] perfected a method in which the cotton is nitrated in a slowly revolving drum, the speed of rotation being afterwards increased so that the acid is forced through a perforated casing, up helical partitions in the drum, where the acid flows over the cotton again. By this device the cotton avoids contact with the air during the nitration process, and so prevents the escape of fumes and the absorption of moisture by the nitrated cotton while still saturated with the acids.

This idea of continuous acid circulation has been extended by J. Selwig,[3] who constructed an apparatus to carry this idea into

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991, 1029; D. R. P. 65540, 1891; 67142, 1892; abst. Ber. 1893, **26**, 125, 471; Wag. Jahr. 1893, **39**, 428; Zts. ang. Chem. 1893, **6**, 232. Swiss P. 4061, 1891. Ital. P. 30264, 1891.

[1] U. S. P. 541573, 1895; abst. J. S. C. I. 1891, **10**, 674; 1892, **11**, 392, 635. E. P. 10747, 1891; 11929, 1900; abst. J. S. C. I. 1891, **10**, 674; 1892, **11**, 392, 635. F. P. 213983; abst. Mon. Sci. 1892, **39**, 271. D. R. P. 64447, 1891; abst. Mon. Sci. 1893, **42**, 862; Wag. Jahr. 1892, **38**, 371; Zts. ang. Chem. 1892, **5**, 622. Swiss P. 2862; Belg. P. 95170. Ital. P. 29852, 1891. Uhlan's W. T. 1896, **3**, 17. See Kube, Chem. Ztg. 1892, **16**, 1616.

[2] E. P. 24561, 1899; abst. J. S. C. I. 1899, **18**, 1180; 1900, **19**, 200, 375.

[3] U. S. P. 764776, 1904; abst. J. A. C. S. 1905, **27R**, 116; J. S. C. I. 1904, **23**, 799; Chem. Zts. 1904, **3**, 738. E. P. 7511, 1904; abst. J. S. C. I. 1905, **24**, 348. F. P. 327803, 1902; 342502, 1904; abst. J. S. C. I. 1903, **22**, 950, 963. D. R. P. 168852; abst. Chem. Zts. 1907, **6**, 47; Wag. Jahr. 1906, **52**, II, 399. Belg. 177833, 1904.

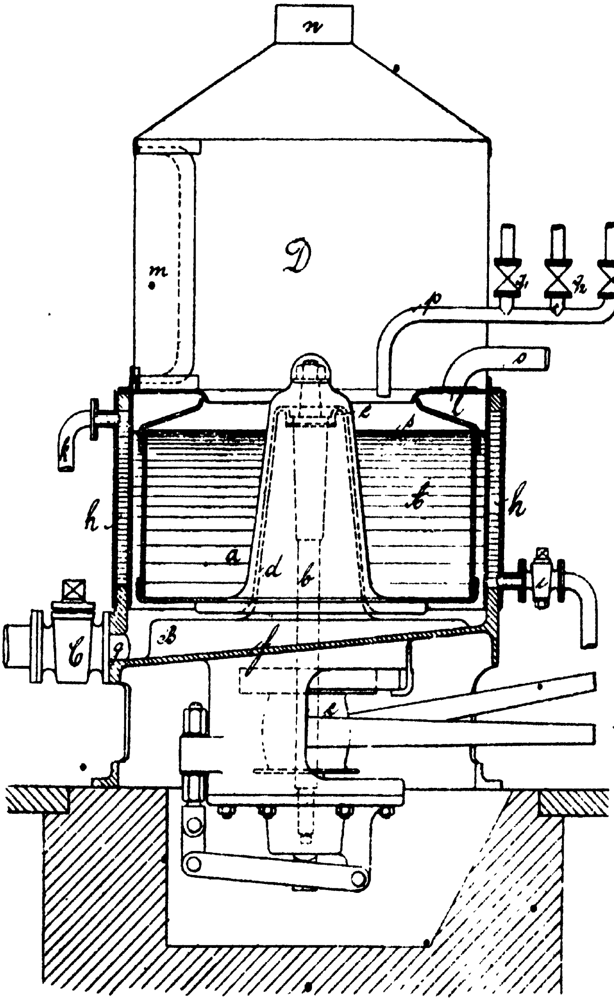

FIG. 151.—SELWIG & LANGE NITRATING CENTRIFUGAL

effect, the details of which are shown in Fig. 152. In carrying out the nitrating processes in the usual manner, it was found

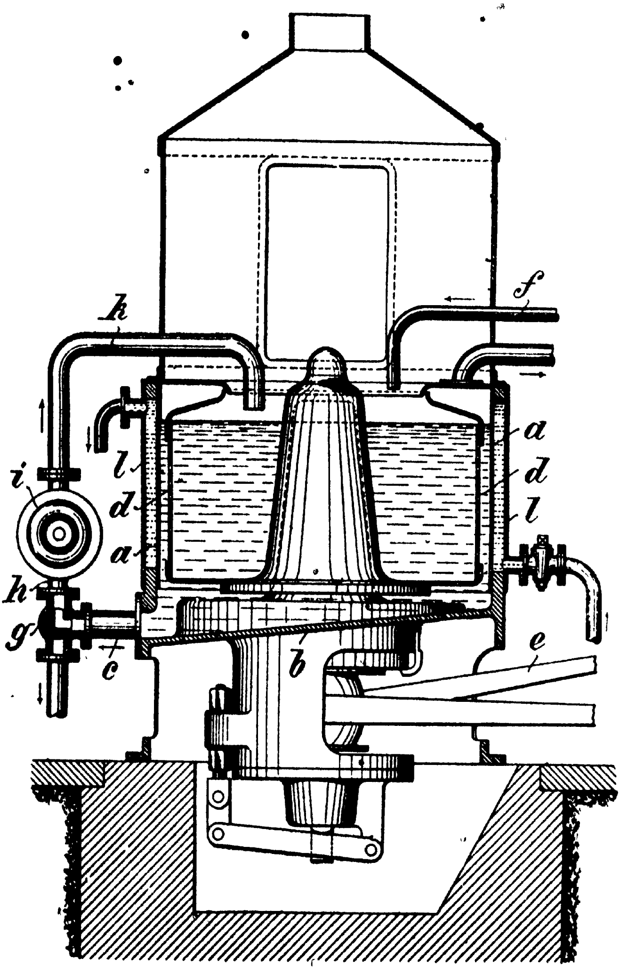

FIG. 152.—SELWIG AND LANGE NITRATING CENTRIFUGAL

difficult, if not well nigh impossible, to insure uniformity in the distribution and progress of the esterification throughout the entire mass of fibrous material treated, not only an unevenly nitrated product resulting in respect to the nitrogen content, but local preheating occurring in various portions due to incomplete agitation, gave different viscosity and solubility results in the finished cellulose ester. Moreover, the cellulose under treatment, as the result primarily of this local preheating, frequently suffered decomposition attended by spontaneous combustion.

To obviate these irregularities, diminish decomposition (fuming off) due to increased generation of heat in different localities in the batch under nitration, continuous circulation of acid was proposed, and has been found a valuable step in advance in cellulose nitration, having resulted in the nearly total avoidance of those conditions which result in self-ignition.

The centrifugal is employed in the following manner, as indicated in Fig. 152, and shown in Figs. 153 and 154. The basket *d* is first filled by means of the pipe *f* with acid, the latter penetrating to the casing *a*, which is provided with an inclined bottom *b* through the perforated wall of the basket, which latter is then charged with the cellulose. When the nitration has reached the

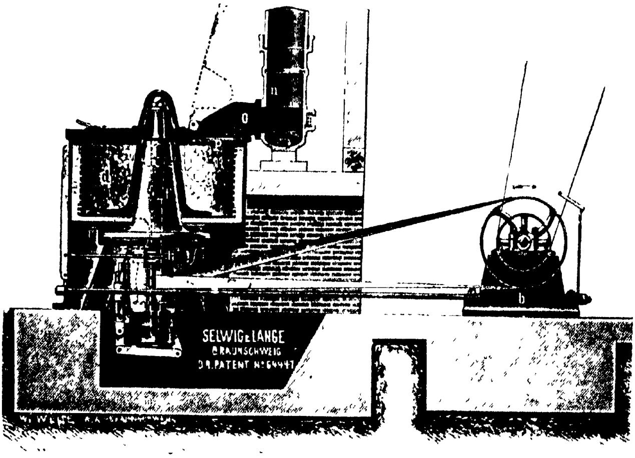

FIG. 153.—SELWIG & LANGE NITRATING CENTRIFUGAL, WITH "ACID CIRCULATION" (SIDE VIEW)

desired stage, the acid is withdrawn from the casing, and the basket rotated by means of the belt *e* to free the nitrated fibers from adhering acid. The casing *a* and basket *d* are provided with means for constantly returning the acid from the casing into the basket, the latter being rotated at 25–35 r. p. m. This slowness of rotation is necessary for finally removing the acid, otherwise the fibers would be too tightly packed against the periphery of the basket and retard the exit of the nitrating acid, as well as preventing the acid from penetrating uniformly the cellulose mass. Where the speed of rotation is too high, there is a tendency for the acid to mount the inner face of the cotton, and ultimately to escape over the upper edge of the basket, the fibers being insufficiently permeated.

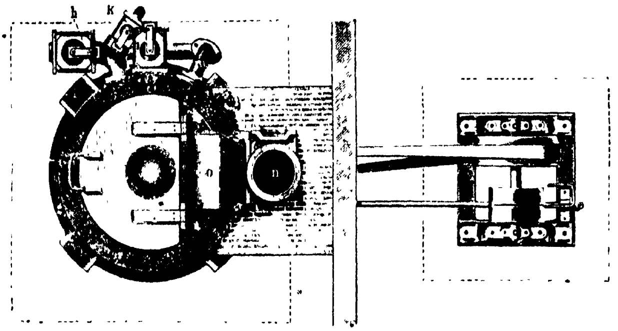

FIG. 154.—SELWIG & LANGE NITRATING CENTRIFUGAL, WITH "ACID CIRCULATION" (TOP VIEW)

In adapting this centrifugal to cotton nitration, two courses may be followed. One consists in combining, with the casing and the basket, an acid pump, or a compressed air ejector *i*, for sucking the acid which has penetrated the fibrous matter, from the lower portion of the casing and pouring it again by way of the pipe *k* into the basket from above near the axis; the basket being either stationary or revolving at a low speed. The other method consists in causing the basket to rotate at 25–35 r. p. m., and simultaneously to catch the acid at the outside of the basket by means of an open channel arranged outside the basket over its upper rim and inclined towards the casing wall, or else by means of a bell-mouthed pipe, the latter being arranged so as to feed the acid back into the central portion of the basket.

It is thus seen that in the machine, the cone is perforated and extended in a ring-like protuberance at the bottom. Very close to the real bottom of the housing a false bottom is installed, which reaches almost to the outer edge and within a very short distance of the ring-like projection on the inner cone. By this means the interior of the cone is brought into communication with the space in the false bottom. When the centrifuge is rotated at the low speed stated, the acid also rotates and sinks in the center while rising on the sides, thus assuming a parabolic form. This causes a corresponding difference in pressure, and the acid circulates from the sides, *down* the sides, and up through the central cone, passing through the cellulose being nitrated in a radial direction. This action also tends to keep the acid cleaner, as by constantly passing through the cotton, the latter acts as a filter, and the loss of cotton suspended in the waste acid is reduced to a minimum.

While at first blush it might appear that the continuous circulation of acids would lead to a loss in nitric acid by fuming, the reverse is actually the case, it having been found in practice that the major portion of the circulation takes place under the surface of the acid, and the construction in no wise interferes with the subsequent removal of the acids by high speed. The earlier machines were made of iron which occasionally split, but at the present time they are constructed of sheet iron, so fabricated that the drum is entirely independent of the cast iron parts.

A second and smaller escape-cock *k* permits the acid in the centrifugal to be collected separately by itself. For the purpose of the circulation of the acid, the middle hollow part of the drum, the so-called drum-cone *t* is provided with a large number of perforations, and lengthened downward in the form of a ring. Above the bottom of the casing, and at a small distance from it, lies a second ring *r*, whose outside edge reaches almost to the side of the casing, while its inner nearly touches the extension of the drum-cone already mentioned above.

There is, therefore, by this arrangement, a direct connection between the interior of the drum-cone and the outside part of the inner chamber of the casing, as will be observed from the cut.

The centrifugal can be made to move quickly or slowly as desired, by putting one or other of the two loose pulleys—which are arranged on the transmission shafting at both sides of the fixed pulley, and which run at different speeds—on to the fixed pulley, the quick-running pulley being then driven by the principal transmission, the slow-moving pulley by a slow-moving intermediate transmission.

In order to exhaust the nitric acid vapors during the process, and to throw off the material undergoing treatment, the centrifugal is connected with a stoneware exhauster by means of the support *o* and the collecting-pot for condensed acid *n* arranged near it. This conveys the vapors to the chimney or to a condensation appliance.

From the above details, it will be seen that by means of the acid-circulating appliance an uninterrupted intimate mixture of the acid is effected, and in such a manner that at a certain fixed moment acid of the same composition and of the same temperature can be made to penetrate throughout the material under treatment. When, therefore, proper raw material of a regular texture is used, a nitrated product is obtained which possesses great uniformity and approximately the same chemical and physical characteristics.

In the older form of nitrating centrifugals, the cast-iron bottom of the centrifugal was also the bottom of the vessel containing the acid, a construction which hindered the work and rendered frequent repairs necessary, for the cast-iron could not resist the effects of the acid for any lengthened period. The new type of centrifugal built by Selwig & Lange is provided with patent acid-holders[1] which are made entirely of steel plate, so that the acid cannot come into contact with cast iron at any part.

At the lowest point of the oblique bottom the escape *q* is fixed, the pressed conical interior of the bottom surrounds the conical upper part *t* of the cast-iron bearing, and the angle-iron riveted on to the bottom of the holder rests on the under frame, to which it is firmly held by means of a few clamp screws. When these are loosened and the conduction pipes screwed off, the entire holder can be easily taken down. In case, therefore, an acid-holder becomes defective, it can be easily and conveniently removed for repairs and its place supplied by a reserve holder. Another advantage consists in the fact that air, which enters through a few holes on the angle-ring fixed on the bottom of the holder, can be sucked through the intermediate chamber between the upper conical part *f* of the bearing and the conical inner part of the holder. The spindle bearing it is thereby well cooled and ventilated and withdrawn completely from the influence of the acid vapors.

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[1] D. R. P. 168852, 174576, 1906; abst. Wag. Jahr. 1906, **52**, II, 399. Chem. Zts. 1907, **6**, 47.

Selwig & Lange[1] have more recently patented[2] an arrangement for feeding paper into the nitrating vessels. The apparatus consists of a vertical stem suspended from a traveling carriage, which can be adjusted over any of the nitrating vessels. At the lower end of the stem is situated a reel of paper, the paper from which passes over a guide roll and between a pair of drawing rolls also carried by the stem. The drawing rolls are operated by means of a belt driven by an electric motor mounted at the upper end of the vertical stem. An oscillatory motion may be imparted to the stem if desired.

In their most recent model of nitrating centrifuge, as illustrated in Fig. 155, provision is made for elimination of the fumes by an efficient draught, shown at the left side of the cut. This is intended to be connected by means of earthenware pipe, and be operated by a stoneware fan. Some criticism has been made as to the inadequacy of this arrangement. When the weather conditions are adverse—i. e., on heavy, muggy and foggy days—it is exceedingly difficult to properly take care of the nitrous fumes during nitration. An ordinary propeller fan with aluminium

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[1] According to their circular the Selwig & Lange's nitrating centrifugals are supplied in the following sizes:

No	External Diameter of Drum	Height of Drum	Capacity		Charge of Cotton	Revolutions per Minute	H P. Necessary	
			of Drum	of Casing			Starting	Running
1	39.4 inch. (1000 mm.)	15 inch. (380 mm.)	56 gal (260 l)	77-88 gal (375-400 l)	22-26½ lb (10-12 k)	about 1000	9-10	2-2.3
2	33.5 inch. (850 mm.)	14.2 inch. (360 mm)	39 gal. (175 l)	82 gal. (ca 255 l.)	14½-17½ lb (6 5-8 k.)	about 1150	7-8	1.7-2

[2] F. P. 409220, 1909; abst. Mon. Sci. 1910, **73**, 295.

blades is much lighter, requires less power to drive, and is equally efficient.

The proportion of acid to cotton is usually about 50 to 1, the charge of cellulose per centrifugal varying with the nature of the cotton being esterified, and the grade in nitrogen per cent.

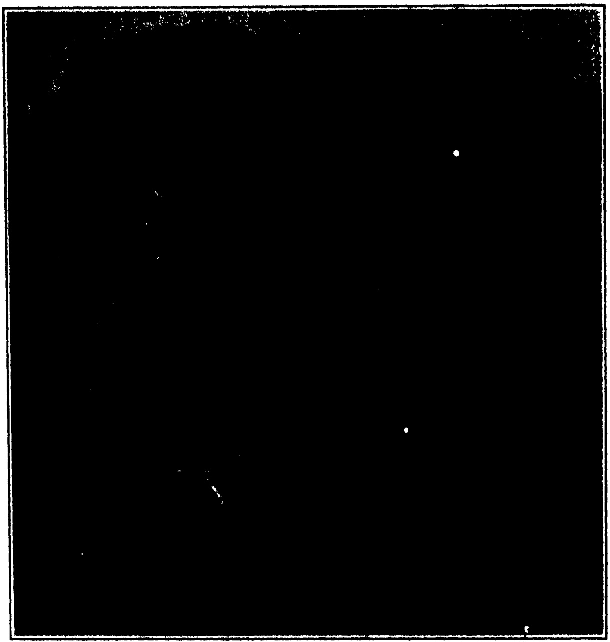

FIG. 155.—SELWIG AND LANGE NITRATING CENTRIFUGAL WITH FUME CONVEYOR ATTACHED

of ester being produced. Ordinarily, a 40-inch basket will comfortably nitrate a 35-lb. batch of cotton. For artificial leather pyroxylins, a yield of 1.3 on the cotton is usually obtained; for celluloid pyroxylin, a yield of 1.38–1.40, and for military guncotton, yields of from 1.50–1.55, a 25–30 minute nitration being made.

Wolfshohl Automatic Cotton Steeper. Another improve-

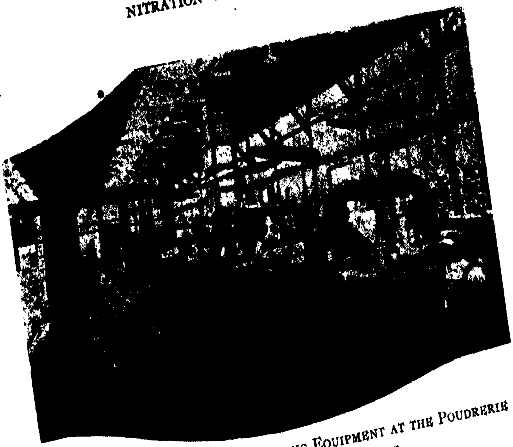

Fig. 156.—Selwig & Lange Nitrating Equipment at the Poudrerie Nationale d'Angouleme, France

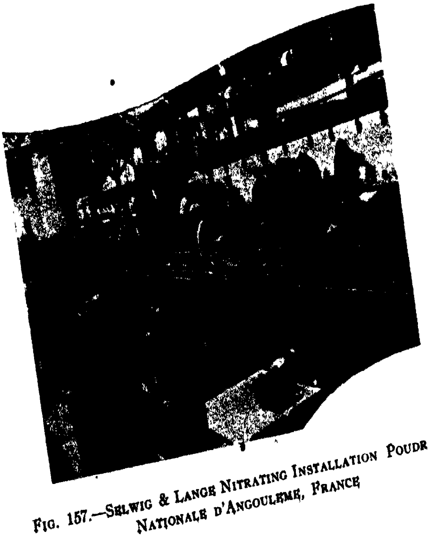

Fig. 157.—Selwig & Lange Nitrating Installation Poudrerie Nationale d'Angouleme, France

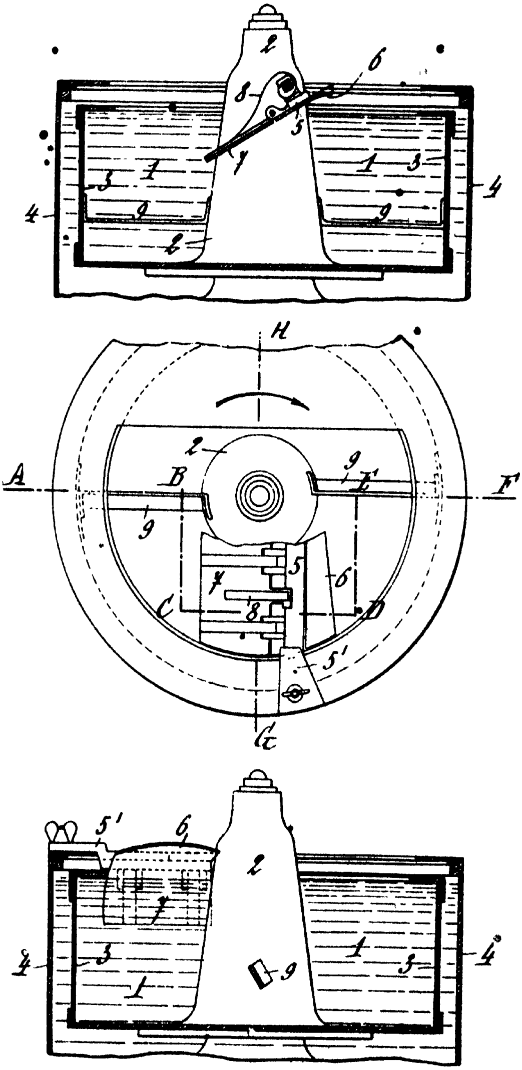

FIG. 158.—WOLFSHOHL AUTOMATIC COTTON STEEPER

ment in nitrating centrifugals consists in the automatic cotton-steeping appliance invented by H. Wolfshohl.[1] Up to the present time the usual method of feeding cotton to the nitrating centrifugal has consisted of one workman throwing the material in small quantities into the apparatus, while another, by means of a long-tined aluminium fork immersed the cotton, the drum filled with the acid charge meanwhile rotating slowly. This method, which is somewhat inconvenient, has been considerably simplified by the arrangement of Wolfshohl, so much so, that the services of the second workman may usually be dispensed with.

The process, which is of mechanical immersion, is shown in detail in Fig. 158, and as attached to a nitrating centrifugal in Fig. 159. The action of the apparatus is explained as follows: When the drum charged with acid slowly rotates, the material to be nitrated after it has been introduced, partakes of the motion of the centrifuge and therefore of the acid contained therein, the result being that the cotton sinks but slowly. If, however, there is immersed in the acid between the central cone and the shell of the drum, a suitably shaped plate, mounted so that it is inclined in the direction of the rotation of the drum, the material to be nitrated when introduced into the drum in moderate quantities, will be retained by the plate or will move with the drum according as the latter is more or less filled with the cellulose.

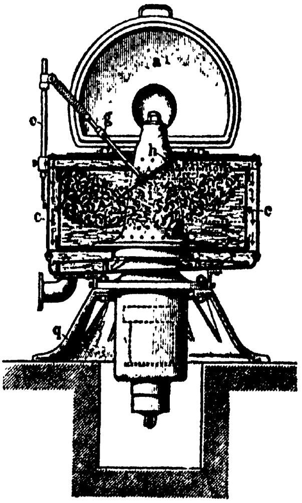

FIG. 159.—WOLFSHOHL AUTOMATIC COTTON STEEPING APPLIANCE FOR NITRATION

In the latter case it will glide under the plate and be pushed downwards, i. e., immersed in the acid. If the completeness of this immersion is to be ensured, the drum must contain one or more devices for compelling the cotton to move with the drum and thus prevent it from piling up and clogging in front of the inclined plate, and in addition, the plate must also be capable of yielding to the upward pressure exerted by the material passing underneath it, particularly when the drum is being charged. This is accomplished by arranging the plate in the form of a flap, hinged at its upper part and urged downwards by a counterweight, as by a spring.

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[1] E. P. 23920, 1905; abst. J. S. C. I. 1906, **25**, 828. F. P. 359625, 1905; abst. J. S. C. I. 1906, **25**, 393; Chem Zts. 1906, **5**, 135. D. R. P 172371; abst. Wag. Jahr. 1907, **53**, I, 473. Belg. P. 188162, 1905.

The apparatus is made entirely of aluminium, and, as shown in the illustrations, consists of an oblique holder *h*, fixed on the cover of the centrifugal by means of a hinged sheet-metal flap *i*, which, filling up the space between the cone of the drum and the casing of the same, dips almost entirely into the acid contained in the drum. By means of a spring rod *g*, which is connected by a joint to the support *e*, the flap *i*, which swings round the upper horizontal edge, is pressed downward, but in such a manner, however, that it can come out somewhat above when pressed from below. In the drum itself is a horizontal tappet of flat aluminium fixed between the cone and the mantle.

Before commencing to feed the centrifugal, the steeping apparatus is fixed on the cover of the centrifugal by means of a pressure screw, and the drum then made to rotate slowly (24–30 revolutions per minute), and in such a direction that its contents move against the under surface of the flap *i*. The cotton or other substance is now thrown into the acid, in front of the apparatus, but not in very large quantities. The contents of the drum are made to partake of the movement by means of the tappet, so that when the cotton is thrown in it also rotates. As soon as it comes to the oblique holder *h* and the flap *i* it is carried right through under both by the strength of the current of the acid, and is therefore thoroughly steeped in the same. The drum is fed until it contains a sufficient quantity of material, whereupon, by loosening the rod *g* from the flap, the whole steeping-arrangement can be taken off, and placed in a stoneware pot near the centrifugal, where it remains when not in use.

Tolhurst Nitrating Centrifugal, as manufactured by the Tolhurst Machine Works, Troy, N. Y., consists of a basket of 40 in. diameter, with a special two speed countershaft, whereby slow speed for nitration and higher speed for acid extraction may be attained, and is shown in Fig. 160. This centrifugal has positive acid circulation, and a high nitrating capacity. No vertical adjustment of spindle is required; the full roller bearings are grease lubricated; the braking and starting levers are in convenient location; the cover is of aluminium with aluminium fume outlet, and contains large acid inlet and outlet.

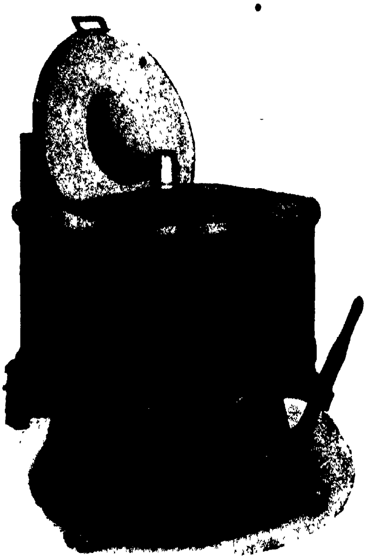
FIG. 160.—TOLHURST NITRATING CENTRIFUGAL

As will be noted from the photograph, the case is especially heavy, and provides ample protection to the belt and bearings from acid splash and fumes.

There is shown in Fig. 161 the Tolhurst acid wringer, designed for those processes where the nitration is conducted in a separate receptacle, the contents being afterwards deprived of nitrating acid by centrifugalization. The apparatus is provided with heavy roller bearings which are flexibly mounted to carry the unbalanced load with the minimum of oscillation. The case is provided with a large fume outlet, removable cover, and spent acid outlet. The baskets may, or may not be removable.

This machine has been extensively employed in conjunction with nitration in a separate vessel, as a pot of boiler iron with acid draw-off valve, the acid being withdrawn after the nitration, the nitrocotton drained for a few minutes, and *then* placed in a wringer for the removal of the maximum of spent acid. It is important to allow the nitrated cellulose to thoroughly drain before centrifugalization.

In addition. this firm manufacture a "finishing centrifugal" shown in Fig. 162, of 40 and 48 in. internal diameter, which is self-balanced, and arranged with annular bottom discharge for handling the neutralized, or partially neutralized nitrocellulose. The discharge opening permits the rapid unloading after centrifuging. These centrifugals may either be driven by countershaft, engine, or motor, and the countershaft or motor may be placed either on the floor or ceiling.

Vacuum Cellulose Nitration. In the older method of the Rheinische Westfalische Sprengstoff A. G.[1] a vacuum tight cast iron or lead tank with perforated false bottom, is connected to a closed acid tank. At the end of the nitration period the acid is sucked off by means of a vacuum into a reservoir, the nitrated cellulose removed, the tank refilled and the process repeated. After removing the vacuum from the reservoir, the acid runs back into the vacuum tank, which is provided with a cooling arrangement.

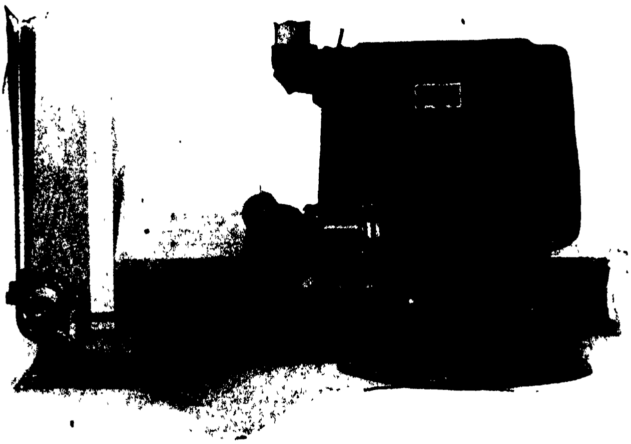

FIG. 161.—TOLHURST ACID WRINGER

In the vacuum nitrating process of L. Dumons[2] and shown in Fig. 163, the cotton is nitrated by producing a vacuum in the midst, and then causing the acid mixture to flow through the cotton into a receiving vessel by means of a vacuum created in the latter, so that all the layers of the cotton are nitrated to the same extent. In the apparatus shown, the cotton is contained in a perforated basket *C* mounted in the nitrating-vessel *B*. The lower part of this vessel is connected to a vacuum vessel *E*, and the upper part to the receiver *A* for the acid. In operation, the cock *R* is closed, and a vacuum first created in the vessels *B*, *E*. The cock *R* is then opened, whereupon the acid in the receiver *A* flows through the cotton into the vessel *E*, from which

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[1] D. R. P. 54077, 1890; abst. Ber. 1890, **23**, 718; Wag. Jahr. 1890, **36**, 539; Zts. ang. Chem. 1890, **3**, 718; Chem. Ztg. 1890, **14**, 1638; 1892, **16**, 277; Chem. Tech. Rep. 1890, **14**, II, 144; Tech. Chem. Jahr. 1890–91, **13**, 153; Jahr. Chem. 1890, **1**, 332; Dingl. Poly. 1891, **282**, 61.

[2] E. P. 14003, 1913; abst. C. A. 1914, **8**, 3860; J. S. C. I. 1914, **33**, 222.

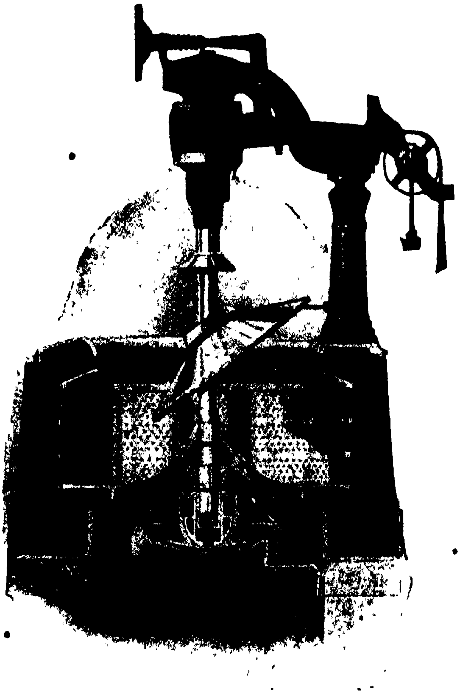

FIG. 162.—TOLHURST FINISHING CENTRIFUGAL

it can be returned to the vessel *A* for re-use after the addition of strong acid. A flue *F* is lowered around the vessel *B* during the nitration process to carry off any fumes arising on raising the cover *D* of the nitrating vessel. The cotton is removed in the basket *C* and emptied into a stream of running water.

The patentee calls attention to the fact that in the ordinary process of cotton esterification, the cellulose to be nitrated cannot

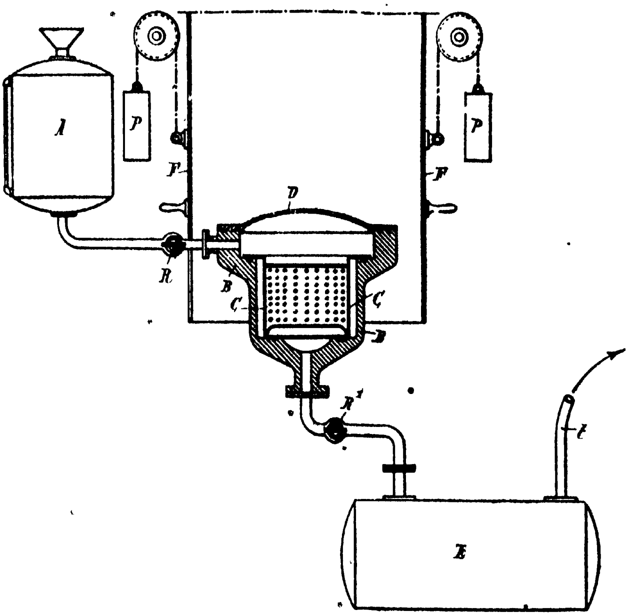

FIG. 163.—THE DUMONS VACUUM NITRATING APPARATUS

all be immersed in the liquid at one and the same time, nor can the liquid act immediately and simultaneously upon the entire mass to be nitrated, as the cotton is and can only be introduced into the apparatus in portions, and with sensible intervals of time. The sections of cotton first introduced into the bath may be nitrated to a greater or higher degree than those portions introduced at a later period, owing to the fact that the latter sections are subjected to nitrating acid lower in nitric and higher in water than the first portions introduced, for as the bath becomes weaker in nitric acid, the nitration of the cotton last introduced can only be effected by the nitrating fluid which has become exhausted from the nitration of the cotton immersed in the earlier part of the process. The above vacuum process is designed to obviate the difficulties above mentioned.

In proceeding according to the method as outlined by Dynamit A. G. Nobel,[1] a batch of cotton weighing up to 50 kilos is evacuated from air, then impregnated with the acid mixture, and immediately passed through cold acid to avoid overheating and maintain the concentration of the acid. The apparatus consists of an iron or earthenware vessel *A*, a nitrator *B*, and a pressure tank sunk in the ground.

The nitrating acid is mixed in the tank *A*, the cotton being placed in compressed form and absolutely dry in *B*, which is then closed and evacuated. The acid is now allowed to enter by opening a valve or faucet, the amount being regulated at will. After the completion of the nitration, the acid is removed by suction, and the nitrocotton emptied and washed in the customary manner.

Other Centrifugal Nitration Processes. In addition to the processes for the centrifugal nitration of cellulose previously described, several other methods have been proposed which embody points of apparent merit, chief among which methods are the following:

In the nitrating wringer as developed by R. Kron[2] and shown in Fig. 164, there is provided a centrifugal perforated basket adapted to be tipped, in combination with a surrounding cylinder or guard, above a liquid receiving or delivering trough, the cylinder being arranged so that it can be moved clear of the centrifugal while this is being tipped.

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[1] D. R. P. 74736; abst. Chem. Centr. 1894, **65**, II, 400; Jahr. Chem. 1894, **47**, 1133; Wag. Jahr. 1894, **40**, 496; Zts. ang. Chem. 1894, **7**, 338; Ber. 1894, **27**, 777.

[2] E. P. 13612, 1891; abst. J. S. C. I. 1891, **10**, 740, 746, 872, 880, 991, 1029. D. R. P. 65540, 1891; 67142, 1892; abst. Ber. 1893, **26**, 125; Wag. Jahr. 1893, **39**, 428; Zts. ang. Chem. 1893, **6**, 22. Swiss 4061, 1891. Ital. P. 30264, 1891.

In the nitration process of A. Vajdafy (D. R. P. 300740, 1915; Abst. Chem. Zentr. 1920, **91**, II, 468; J. S. C. I. 1920, **39**, 429-A) the material is kept in motion so as to absorb the acid in a gradual, continuous and uniform manner, and is then pressed to yield a product containing only 70% of acid. The rotary nitration apparatus, which is mounted on an inclined shaft and gradually diminishes in size towards the top, is provided with spirally arranged, internal ribs.

The J. Alliott centrifugal comprizes a perforated basket surrounded by a casing[1] which will retain a sufficient quantity of liquid in the basket when it is stationary, and permit the liquid to flow from the basket under the action of centrifugal force when it is rotating. The casing takes the form of a frustrum of a hollow cone, and rotates within the basket.

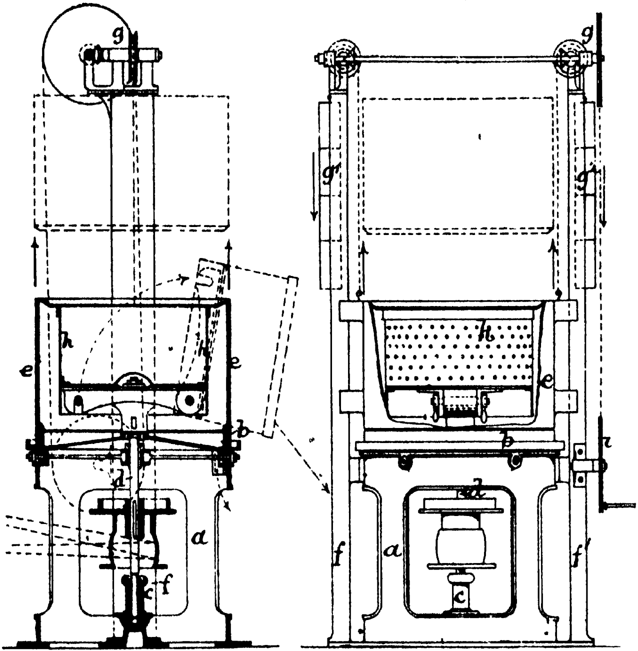

Fig. 164.—Kron Nitrating Centrifugal

The apparatus of H. Risler[2] is a nitrating centrifugal for wringing the spent acids from the nitrated material, and is built with perforated segments which are placed under the edge or flange of the centrifuge drum, the object being to cover the nitrocellulose and prevent its flying out. In the nitrating apparatus of the Vereinigte Eisenhütten u. Maschinenbau A. G.,[1] the cover is held in place by means of springs so that it is lifted in the event of undue pressure being developed in the nitrating vessel, but returns to its normal position as soon as the pressure is relieved. An annular hood, attached to the cover and to the rim of the nitrating vessel, is arranged over the joint, so that in the event of an explosion in the nitrating vessel, any flame jets escaping are directed downwards.

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[1] E. P. 3177, 1902; abst. J. S. C. I. 1903, **22**, 287.

[2] F. P. 454849, 1913; abst. C. A. 1914, **8**, 1361; Chem. Ztg. Rep. 1914, **38**, 9.

The Sudenburger Maschinen Fabrik[2] manufacture a nitrating vessel with conical sidewalls which is fastened to the axis of a centrifuge, and contains another vessel with holes serving for the reception of the cotton to be nitrated. The whole is arranged in a closed space to prevent attack by acid vapors, and is provided with an efficient vapor removing system. The bottom of the space is closed by a tight membrane while the apparatus is stationary, thus allowing the acid to flow away when the vessel is in rotation. The T. Quiller[3] and the Davidsen[4] processes are similar, as well as the tipping centrifugal design of M. Delpy.[5]

Gebrüder Heine have also constructed centrifuges with circulating acid device on a novel principle,[6] in which the acid returns through the holes in the inner side of the drum. The circulation of acid is brought about and maintained by means of a ring which surrounds the drum in a spiral screw thread form.

Another type of centrifuge constructed by this firm especially for purposes of cotton nitration,[7] has a rotating drum with double walls, the inner wall perforated, the outer wall not. The material to be nitrated is placed in the inner drum as usual, the double drum being filled with acid in the customary manner. When the drum rotates with sufficient velocity, the level of the acids will assume a parabolic form. Several removable scoops pick up the acids in the space between the perforated and imperforate drum, which is conducted through a common centrally located tube back to the bottom of the apparatus, from which it re-enters the drums through the perforations at the inner side. All the acid is thus compelled to circulate, and high efficiency is attained. Afterwards the scoops and central tube are swung aside and the acid centrifugalized at high speed.

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[1] D. R. P. 288362, 1915; abst J. S. C. I 1916, **35,** 558, Chem. Ztg. Rep. 1915, **39,** 494; Wag Jahr. 1916, **62,** I, 25; Zts ang. Chem. 1915, **28,** 632.

[2] D. R. P. 58381, 1890; abst. Ber 1892, **25,** 240, Wag Jahr. 1891, **37,** 430; Zts. ang. Chem 1891, **4,** 682.

[3] Norw P. 21879, 1910; abst Chem Ztg 1912, **36,** 115.

[4] F. P. 255563, 1896.

[5] D. G. M. 511610, 1912. E. P. 8992, 1912, abst. C A. 1913, **7,** 3425; J. S. C. I. 1912, **31,** 786

[6] D. R. P 120597; abst Zts Schiess Spreng. 1910, **5,** 438. In D. R. P. 165225, 1903; abst J. S. C I 1905, **24,** 457; Wag. Jahr. 1904, **50,** I, 345; Chem. Ztg. Rep. 1905, **29,** 104, Chem Zts 1905, **4,** 197, 292, the outlet channels for the acid are provided with overflow tubes

[7] D. R. P. 202489, abst. Chem. Ztg. Rep 1908, **32,** 579; Wag. Jahr. 1908, **54,** I, 432; Zts. Schiess. Spreng 1908, **3,** 315. In the Gebr. Heine and Färbereien v. J. Schetty Söhne, D. R. P 270571, 1912 (Add to D. R. P. 260177; abst. C. A. 1913, **7,** 3236; 1914, **8,** 2490; Chem. Ztg. Rep. 1914, **38,** 226; Wag. Jahr. 1914, **60,** II, 352). The centrifuge is especially adapted for dyeing, bleaching, washing and nitrating textile materials.

This firm also builds nitrating centrifugals of glazed earthenware, cemented into steel drums to prevent rupture. In this apparatus the lower bearing is of ball thrust,[1] thus automatically taking the strain off by means of a hydraulic arrangement, lubrication being by automatic oil circulation. The drive is from underneath by a single belt.

In one of the models of nitrating centrifugals as manufactured by C. Haubold, and used extensively in Germany and elsewhere, each part of the machine which can come in contact with the nitrating acid is constructed of stoneware. In one preferred constructional arrangement, the drum is composed of two walls, the outer one solid, and the inner one perforated. The space between the two is closed at the top, and widens conically at the bottom, where the acid removed by wringing, and is withdrawn by several openings normally closed by stoneware balls. When the machine is in rotation, the centrifugal force dislodges the balls, and allows the acid to run off, the balls automatically returning to their seats as the machine stops. The stoneware portion is built into an iron body so constructed that it can be tightened by bolts in two directions, the space between it and the stoneware parts being filled in with a cement which will indefinitely remain in elastic condition. The pressure against the inner stoneware parts is so adjusted as to be greater than the calculated outer pressure due to centrifugal force, in order to preclude the possibility of bursting the stoneware drum of the centrifugal.

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[1] D. R. P. 164638. O. Gründlich (Zts. Schiess. Spreng. 1910, 5, 352, 413, 434, 458, 478) has given a detailed and exhaustive résumé of nitrating centrifugals, with 28 cuts.

The acid thrown off when the centrifuge is in motion, is caught in a stoneware ring with a higher outer wall, and runs off through stoneware cocks. If it is desired to run acid out of the centrifugal while standing still, the stoneware balls can be lifted from their seats by means of an aluminium wire. When used only as an acid removing wringer, the balls may be entirely dispensed with.

Another nitrating and acid removing centrifugal type constructed by C. Haubold is of unusually heavy construction, the drive being built on the same frame as the machine. The outer shell may be rigid, or made demountable, the advantages being that at the end of the nitrating operation, the filled drum can be lifted out and replaced by another full one, thus saving time. The connections of the drum to the rotor are so arranged that it automatically disengages on lifting. The outer shell is made hollow to permit of heating or cooling. Acid fumes are removed by a S-shaped pipe connected to the shell, so arranged as to prevent the carrying away of fine particles of nitrated cotton, or of acids.

An important point in connection with any nitration process, but especially in centrifugal esterification, is the proper removal of the nitrous vapors from the nitrating chamber, in all cases where the vapors are not removed from the closed nitrating apparatus by direct conduit pipes. Many factories have louvres on the roof, but they are usually defective in efficiency, and the fumes soon corrode the iron framework of the building, aside from the detrimental effect on the neighboring vegetation where the acid may be precipitated by the moisture. Other plants have arranged large hoods leading to a chimney with steam suction in the stack to effect circulation. Furthermore the acid vapors represent money, in many instances economical to try and recover.

A rational method is to remove the vapors by stoneware suction fans, and conduct the fumes, if desired, through towers packed with a cheap filling material, down which trickles a fine stream of water. Selwig and Lange build fans with aluminium casing and fanwheel.[1]

The various accidents which have been reported in connec-

[1] D. R. G. M. 216323. The Vereinigte Tonwarenwerke (D. R. P. 161933; abst. Wag. Jahr. 1905, **51**, I, 450; Chem. Ztg. Rep. 1905, **29**, 307;

tion with the operation of cotton nitrating centrifugals, have only emphasized the extreme care which manufacturers of this apparatus should bestow in determining that their machines possess the maximum of strength and safety.[1] In one instance which may be cited,[2] the suggested possible explanation of the cause of the decomposition, was that drops of condensed water from the centrifugal cover fell into the guncotton, or that pieces of wood or hardened lumps of cellulose led to local preheating which was not readily dissipated. Kubierschky[3] has designed the construction of a continuously operating nitrating apparatus, automatically regulated, alleged to overcome the dangers found in the other types.

In the nitrating centrifugal as developed by the Vereinigte Tonwarenwerke,[4] the perforated insert of the centrifugal drum has walls that are concave towards the outside of the drum, and resting against the bottom of the drum, the upper edge being retained by the sloping outer walls. By tightening up screws, the stoneware part is put under compression so that there is a tendency to buckle inwardly, thus compensating any outer pressure induced by the centrifugal force when the machine is in motion. Elastic rings conveniently placed, serve to minimize any mechanical shocks which would tend to break the stoneware parts. Construction is such that no acid can come in contact with the metal parts.

The Thomson Displacement Process of cotton nitration, devized by J. M. Thomson and W. T. Thomson, is designed for the nitration of cotton for a wide variety of uses. In England, where the process was perfected and first patented in 1903,[5] so-called "guncotton proper"—those cellulose nitrates of highest

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Zts. Schiess. Spreng. 1906, **1,** 16) have patented an automatic device for the opening of the outlet valves of nitrating centrifugals, wherein the valves are opened by means of a special device operated by centrifugal power.

[1] Ann. Rep. H. M. Inspect Expl 1886, 20, 32, 53, 99.

[2] Anon., Zts. Schiess. Spreng. 1915, **10,** 46; abst. C. A. 1915, **9,** 1248.

[3] Anon., Chem. Ztg. 1911, **35,** 1440; abst. C. A. 1912, **6,** 804; J. S. C. I. 1912, **31,** 92.

[4] D. R. P. 159227; abst. Wag. Jahr. 1905, **51,** I, 449; Mon. Sci. 1907, **67,** 19; Chem. Zts. 1907, **6,** 48.

[5] E. P. 8278, 1903; F. P. 364981, 1906; no U. S. P. granted; abst. J. S. C. I. 1904, **23,** 560; Mon. Sci. 1904, **23,** 733; Arms Expl. 1904, **12,** 84. D. R. P. 172499; abst. Mon. Sci. 1908, **69,** 160; Chem. Centr. 1906, **77,** II, 840; Jahr. Chem. 1905–08, II, 973; Wag. Jahr. 1906, **52,** I, 475; Zts. ang. Chem. 1906, **19,** 1056; Zts. Schiess. Spreng. 1906, **1,** 261; Kunst. 1912, **2,** 35.

nitration and insoluble in ether-alcohol with nitrogen content of around 13.5%, and intended for blasting gelatin and torpedo work—having been used exclusively in England at Waltham Abbey since August, 1905. In the United States this process was first tried on an experimental scale in February, 1908, actual production being commenced some three weeks later,[1] at the Government Picatinny Arsenal, Dover, N. J., Colonel Odus C. Horney, commanding, where it has been in operation continuously since, this being the only place in the United States, to the author's knowledge, where this process has been carried on.[2]

In the original specification of the inventors, the patent claims are based upon the discovery made by them, that the acid extraction and preliminary washing operations in cotton nitration may be combined by removing the acids from the nitrated cellulose directly by displacement without the employment of either pressure, vacuum or mechanical appliances, and at the same time securing the minimum dilution of the acids. They also observed that if water be carefully run on the surface of the acids in which the nitrocellulose is immersed and the acids slowly drawn off at the bottom of the vessel, the water displaces the acid from the interstices of the nitrocellulose with no undesirable rise in temperature, and with but little dilution of the nitrating acids. By this method the maximum acid is recovered in condition suitable for concentration and re-use, and the volume of water required for the preliminary washing materially reduced.

This method has been adapted to the preparation of a pyrocollodion powder at the Picatinny Arsenal above referred to, with a nitrogen content of 12.5%–12.7%, and practically complete solubility in ether-alcohol. At the present time a large series of four pans each are in daily operation, each pan consisting of a cylindrical stoneware vessel (see Figs. 170–172), constructed with a perforated stoneware false bottom which is removable, and under which is a cock at the lowest point for running off the liquid.[1] The nitrating acid at a temperature of 28°–30°, and containing nitric acid 21%–22%, sulfuric acid 63%–64%, is run by gravity[2] into the pans, 700 lbs. in each.[3] The cotton—20-lb. charges for each pan—is brought into the nitrating house in sealed cans, with moisture content less than 1%, and at a temperature at least as high as the nitrating acid in which it is to be immersed.[4] The cotton is immersed in the acid in small portions at a time, the entire operation requiring about fifteen minutes. When the charge of cotton has been entirely immersed, the five-section perforated stoneware top plates are placed over the cotton, care being taken that all pieces of cotton are under the surface of the acid. A film of cold water[5] is then immediately flowed over the surface of the top plates to a depth of about one inch[6]

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[1] Through the courtesy of Colonel Horney, the then commanding officer, the author was permitted to see the process in operation, and from whom much of the data contained herein was obtained. The description of the English method has been taken principally from an article by F. Nathan, J. S. C. I. 1909, **28**, 181; Chem News, 1909, **99**, 136, 152, 159; see also "Arms and Explosives," 1906, **14**, 77.

[2] The nitrating acid enters the pans *A*, from underneath, *B* being the one-piece perforated segmental plate placed on the bottom of each pan before the introduction of the cotton. A hood, shown faintly in the background is placed over each pan during introduction of the cotton into the nitrating acid, and by means of the flue *D*, the fumes from two pans are carried downward by suction and out of the building. A fan is located in the roof of the building which forces pure air through the apertures shown at *H*. The stream of water issues from the quarter-inch rubber hose *F* which is kept in position by means of a weight, such as a piece of lead *G*. The nitrated and washed cotton is shown at *E*. When the entire surface has been covered with a thin film of water, fuming ceases. After nitration has been completed, the spent acid is withdrawn and cold water run in so gradually that no dangerous rise in temperature takes place.

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[1] Four pans are usually spoken of as unit and are nitrated and emptied together. In nitrating such a unit the services of six men are required to immerse the cotton in the nitrating acid, one man to immerse the cotton for each pan, and one man for each two pans, who places the cotton onto the acid for the immersion by galvanized iron forks. A single-piece hood constructed of wood, but impregnated with paraffin oil and coated with a high congealing-point wax forms the hoods, each hood having an opening on opposite sides for the delivery of the cotton and for the submerging of it. The top of the hood, directly over the center of each pan, contains a window, over which is suspended an electric light to better light the interior of the pans during the preliminary immersion. Exhaust pipes are also provided for the withdrawal of fumes.

[2] Various devices are in operation for heating the acid to the desired temperature before introduction of the cotton. In one method the acid circulates through pipes in a steam jacket or hot-water tank. Perhaps as simple and efficient as any is to encase the delivery pipe with a larger pipe containing steam connection, when by admitting steam at a given pressure, and running the nitrating acid through the inner tube at a determined volume, heating of the nitrating acid is practically automatic.

[3] In J. S. C. I. 1909, **28**, 181, a charge of 600–650 lbs. is recommended for the production of cellulose nitrate of highest nitration, a 29-lb. charge of cotton being used.

[4] From five to ten minutes is required to run in the nitrating acid per pan, depending on the force of gravity and the diameter of the entering pipe.

[5] A small stream for a quarter-inch ordinary gas tubing hose is sufficient.

[6] Thomson in their original patent (l. c.) suggest the use of sulfuric

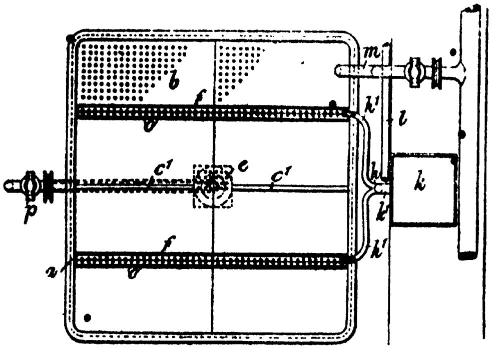

Fig. 165.—Thomson Displacement Apparatus for Cotton Nitration

a, Tank; *b*, False bottom; *c'*, Ribs; *e*, Grid; *f*, Troughs; *g*, Aprons; *h* and *h'*, Pipes to Troughs; *m*, Pipe to Nitrating Acids; *o*, Perforations of Troughs; *p*, Cock for Removal of Acid.

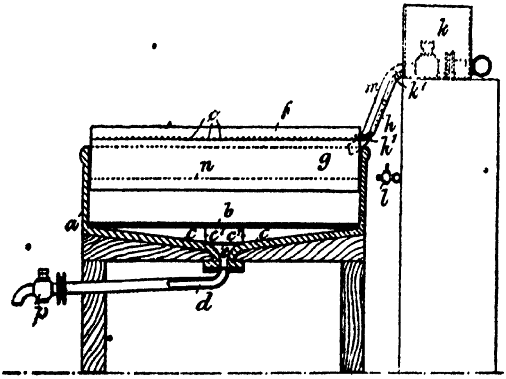

Fig. 166.—Thomson Displacement Apparatus for Cotton Nitration (Sectional Elevation)

a, Tank; *b*, False Bottom; *c'*, Ribs; *d*, Drainage Outlet; *e*, Grid; *f*, Troughs; *g*, Aprons; *h*, *h'*, Pipe and Branches to Troughs; *l*, Water Supply Pipe; *m*, Pipe Leading from Nitrating Acids; *o*, Perforations in Trough; *p*, Cock to Remove Spent Acid.

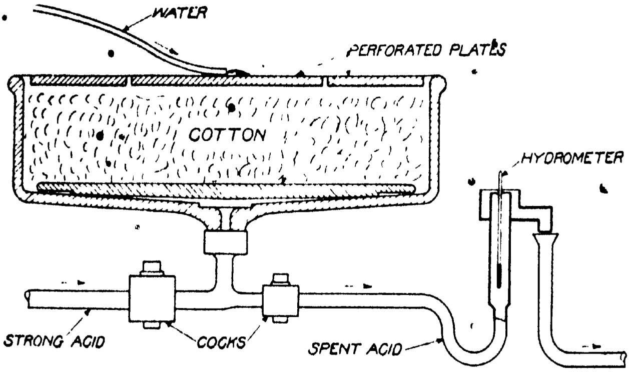

FIG. 167.—THOMSON DISPLACEMENT NITRATOR

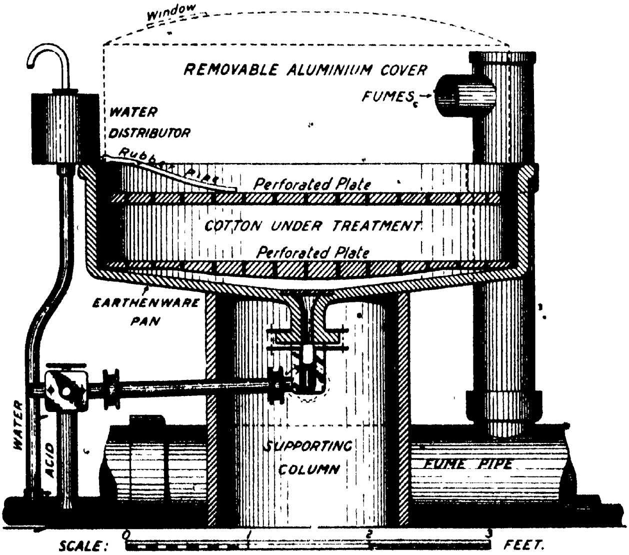

FIG. 168.—THOMSON DISPLACEMENT NITRATING PAN

in order to seal the nitrating acid and prevent fuming. The hoods which are placed over the pans during immersion of the cotton[1] are now removed, the cotton remaining soaking in the nitrating acid for periods varying from 1-2.5 hours, depending on the physical results in the nitrocotton desired. At the expiration of the time in which the nitration is considered completed, the cock leading to the waste pipe is gradually opened, the waste acid allowed to flow away from the nitrated cotton at the rate of about 17 lbs. per minute, the volume of fluid in the pan being maintained by running cold water in on the top plates through the distributor. This displacement of acid by cold water is continued until the major portion of the acid has run out, the water following the acid through the nitrocotton with but little appreciable mixing, this displacement requiring about forty-five

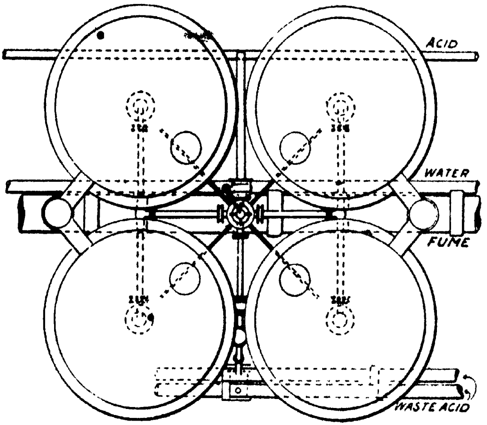

FIG. 169.—A UNIT OF FOUR THOMSON DISPLACEMENT PANS (from *Arms and Explosives*)

acid for sealing where the higher nitrated cottons are being prepared. In some cases the method may be carried out in an ordinary centrifugal, using the latter to effect preliminary drying after acid extraction. This has the advantage over the usual method of working the ordinary centrifugal nitrating apparatus, because the acid being removed from the centrifugal is so gradual that practically all danger of firing and "fuming" disappears, and a greater proportion of waste acid is recovered.

[1] The hoods may be transported around the nitrating room by means of a traveling crane.

minutes.[1] The water displaces the mixed acids so gradually that the temperature of the nitrating acid in the pans is not raised. The waste acid passes out of a 3-inch pipe by means of overflow into a larger pipe, and in this 3-inch pipe floats a hydrometer, whereby the concentration of the acid may be observed.[2] The cotton after the water has been allowed to drain away is shoveled into trucks, either with aluminium forks or preferably with wooden shovels,[3] and wheeled to the wash house, the pans washed out and the operation repeated.[4]

This system of manufacture offers many advantages over other methods of cotton nitration, among which may be mentioned the following as the more meritorious points:

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[1] The patentees found that the rate of displacement exerts a considerable influence on the properties of the resulting nitrated celluloses, and affords a means of regulating the temperature of displacement, the rate found suitable being about two inches per hour when treating highly nitrated celluloses. It is especially essential in this process that the water used be thoroughly filtered, for if the clarification of the water has been inefficient, when the top plates in the pans are removed at the close of the nitrating process, the nitrocotton immediately under the hose which supplied the water will be found in various stages of discoloration, or perhaps a dark precipitate deposited, the cotton acting like a filter to separate the solid particles. Although these particles (if present) are supposed to be removed in filtering the block of gelatinized cellulose nitrate through the "macaroni" hydraulic press, filtration of the water used in displacement through sand or sponge filters is always desirable

[2] There is more waste acid separated and reclaimed by this process than can be utilized for fortifying purposes indefinitely, the spent acid accumulating. In order, however, to obtain the desired amount of spent acid of maximum concentration, various methods have been tried to divide the waste acid into definite fractions The specific gravity of the strongest acid as it leaves the pans and at the temperature (about 32°) is about 1.7 By now separating as the first fraction a volume of spent acid required to make up the next day's run of acid, using the strongest commercial acids obtainable, and for a second fraction, all that portion not required for strengthening, but yet sufficiently strong so as not to attack too powerfully the transportation containers, seems to be the most economical solution of the problem of spent-acid recovery and utilization It has been found that a spent acid of sp gr. much under 1.4 attacks iron so readily as to be inadvizable for reshipment, and it is usually run into the sewer The charge of nitrating acid for a pyrocollodion nitrocellulose usually consists of three portions (1) The spent acid from previous nitration (2) Sulfuric acid 98% absolute H_2SO_4 (which in winter has about 1% of nitric acid added to it to prevent freezing by the formation of monohydrate crystals) and (3) a mixture of nitric acid 52%, sulfuric acid 45%.

[3] The so-called potato shovels, made entirely of wood

[4] In the Austrian method of cellulose nitrate manufacture (G. MacDonald, "Arms and Explosives," 1909, p. 38) raw cotton is immersed in an acid mixture forty-eight hours, then placed in running water four to eight weeks until free from acid. In the French method, cotton is immersed in an acid mixture for one hour and then immersed in running water for one hour. The remaining acid is subsequently neutralized by a solution of potassium carbonate.

(1) The displacement process takes the place of the processes of dipping, digesting in pots, acid centrifugalizing, immersing and hydroextraction.

(2) The actual dipping of the cotton is a much less laborious operation — the heavy labor of squeezing out the acid is done away with, while the absence of fumes makes the work much less disagreeable and more healthful. Fuming by this process is almost unknown, and injuries to workmen from acid splashing very infrequent.

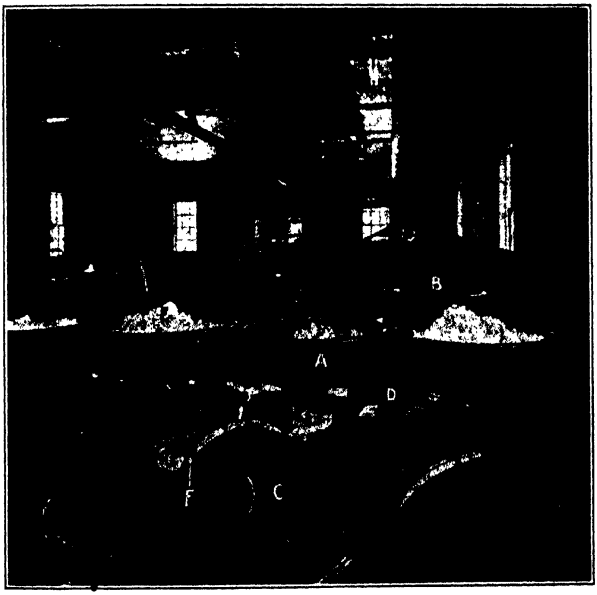

Fig. 170.—The Thomson Displacement Process for Cotton Nitration, at Picatinny Arsenal, Dover, N. J.

(3) Loss of nitrocotton due to decomposition in the digesting pots and acid centrifugals and consequent inconvenience and danger to workmen from nitrous fumes are done away with, and

FIG. 171.—THOMSON DISPLACEMENT NITRATION IN FRANCE

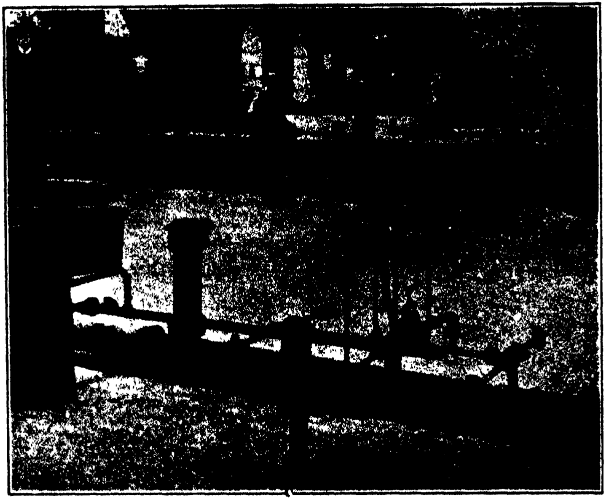

FIG. 172.—PLUMBING INSTALLATION FOR DISPLACEMENT PLANT (from *Arms and Explosives*)

the heavy loss from breakage of pots and lids avoided. The experience of a number of years at Picatinny and at Waltham Abbey have shown that the earthenware pots are very lasting.

(4) The fumes incident to loading and unloading acid centrifugals and immersing are avoided.

(5) The quantity of acid lost is much reduced, and this reduction means less pollution of the discarded wash-waters.

(6) The recovered waste acid is much cleaner, a point of great importance from the point of view of revivification and concentration.

(7) The mechanical loss of nitrocotton in the acid and water centrifugalizing processes and in the immersing processes is avoided.

FIG. 173.—VIEW SHOWING ARRANGEMENT OF UNITS IN ROWS (from *Arms and Explosives*)

(8) A more thorough preliminary washing is obtained with an expenditure of about one-fifth of the quantity of water, and less boiling, with consequent consumption of steam, is required in order to reach a given standard of purity.

(9) Great saving in power is gained by the abolition of the acid and water centrifugals, and in the reduction in the quantity of water which has to be pumped.

(10) Renewals of plant and repairs to plant and buildings are said to be exceedingly low.

(11) The number of hands employed for any given output is much less—the total cost of labor being reduced by two-thirds.

(12) The yield is improved. At Waltham Abbey it is given as 170% (probably theoretical). At Picatinny with a 12.6% nitrogen it is between 151%-152%.

(13) A more stable nitrocotton, of more uniform nitrogen

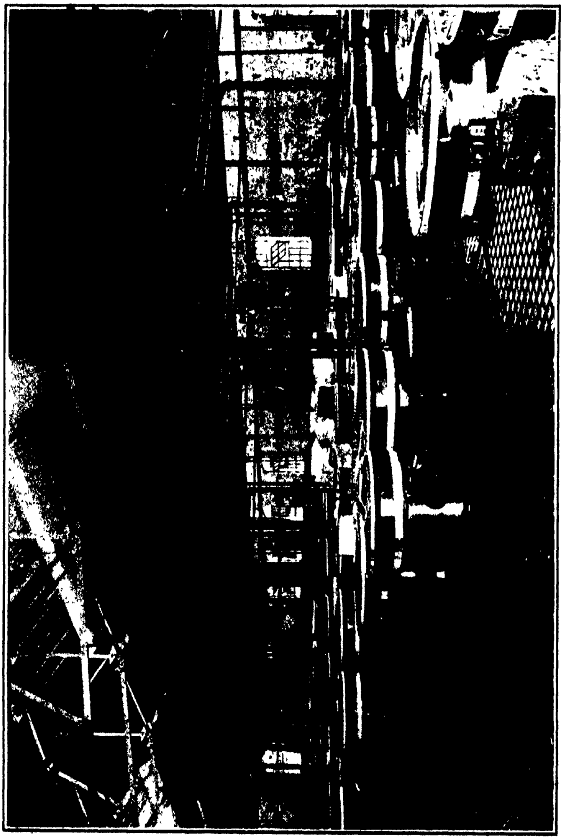

FIG. 174.—THOMSON DISPLACEMENT NITRATION PANS

content, is stated to be produced. It is also far cleaner and contains notably less mineral matter.

(14) According to G. Lunge the loss of concentrated acid is only 14% of the weight of cellulose nitrate as compared with a loss of 150% by the older processes.

G. Mac Donald[1] has examined the spent acids issuing from the Thomson displacement process for cellulose nitration and has found that as the displacement proceeds, the percentage of nitric acid in the waste acid first falls slightly, then rises distinctly and finally falls, whereas the ratio of nitric to sulfuric acid, after a very slight initial falling, rises steadily until the end of the displacement period. This phenomenon is explainable only as due to a partial denitration of the nitrocellulose and the evidence of decomposition of the more unstable products to a greater extent than that from normal cellulose nitrate. These results are clearly shown in the following table:

	Time of Flow (Min.)	Weight Acid	Composition			
			H_2SO_4	HNO_3	HNO_2	H_2O
Mixed acid		2750	70.82	21.26	0.53	7.57
Acid for regenerating	145	2033	72.93	17.57	0.56	8.94
Acid to be denitrated	25	324	71.55	16.46	0.56	11.43
	8	86	61.93	18.26	0.45	19.36
and concentrated	3	35	51.56	18.86	0.34	29.72
	3	33	42.22	17.99	0.24	39.55
	7	83	21.91	11.83	0.16	66.07
	7	71	4.24	3.61	0.15	92.00
Waste acid	45	589	0.48	0.44	0.10	98.98

RISE OF TEMPERATURE

Minutes	Temperature
15	14.0°
30	16.0
45	17.0
135	22.0
150	23.0
155	24.0
160	25.7
165	26.5
170	26.5

According to Mac Donald, 70% of the mixed acid is recovered for regeneration at the speed of 14 pounds per minute, the actual loss of acid being only 0.4% of the total or 0.08 part to one part of guncotton produced. The water consumed equals one gallon per two pounds of guncotton, the proportion of mixed acid to cotton being 34.37% to 1, whereas in the centrifugal processes the usual ratio is fifty to one. The product produced contains on the average 13.0% nitrogen compared with 13.1% to 13.2% in the centrifugal method. He points out that with the latter method, the loss of acid equals approximately 2 gallons per kilo of guncotton produced.

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[1] J. S. C. I. 1911, **30**, 251; abst. Zts. Schiess Sprengs 1911, **6**, 389; C. A. 1911, **5**, 1839; Rep. Chim 1911, **11**, 255, Chem Zentr. 1911, **82**, I, 1902; Chem Ztg 1911, **35**, 281

G. Lunge[1] has found that the water completely displaces the mixed acids from the nitrating bath without appreciably raising the temperature or diluting the acids, and that the latter can be used over again with less fortifying, while the nitrating material does not require as much washing as in the older processes. Lunge summarizes the advantages of this process as follows: saving of time and labor, there being no nitration pots or centrifugals to break or get out of order; absence of fuming; simplicity of apparatus; loss in concentrated acid of only 14% of the weight of the cellulose nitrate obtained, compared with a loss of 150% in the other process; requiring much less preliminary washing; and loss of acid in wash water, and absence of fuming which is better for the health of the workmen.

M. Delpy[2] states that as the result of his experience with the Thomson process he has not succeeded to any extent in replacing even a part of the centrifugal nitrating system. He cites an instance in which a collodion plant was altered from the pot system to the Thomson process, wherein 28 units designed for a daily yield of 3,000 kilos, gave only a maximum of 1700 kilos of nitrated cellulose. This system was then replaced, so he says, by seven nitrating centrifugals with entirely satisfactory results. In opposition to the claims of Thomson for his method, the following disadvantages of the displacement process are given as shown from practical operation of the plant above mentioned: First, increased trouble from acid fumes; second, high cost of repairs; third, large losses of acid from breakdowns in acid leads, etc.; fourth, increased number of operators required (18 as compared with 8 with the centrifugal system); and fifth, greater ultimate losses of acid than with centrifugal nitration. In view of the most thorough and practical investigation and commercial use of this process both at Picatinny Arsenal in the United States and in England, the above objections should be accepted *cum grano salis.*

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[1] Zts. Schiess. Spreng. 1906, **1,** 2; abst. Chem. Centr. 1906, **77,** I, 714; Jahr. Chem. 1905–08, II, 974; Wag. Jahr. 1906, **52,** I, 487; C. A. 1907, **1,** 1622; Meyer Jahr. Chem. 1905, **15,** 356. See also O. Guttmann, Chem. Zts. 1905, **4,** 197.

[2] Zts. Schiess. Spreng. 1912, **7,** 237; abst. J. S. C. I. 1912, **31,** 662; C. A. 1912, **6,** 2842; Chem. Zentr. 1912, **83,** II, 977.

According to a recent article,[1] further evidence of the superiority of the centrifugal method over the displacement process for nitration is found in the fact that sixteen centrifugals of recent type have lately been installed in the French factory at Moulin Blanc as the result of a report of a French Investigating Commission.[2]

The process of C. Claessen[3] is quite similar to that of Thomson. In this, after the nitration is finished and the acid has been separated, sulfuric acid is injected into the rotating drum of the centrifuge containing the nitrating material and the sulfuric acid subsequently displaced by water.

Sulfuric acid being by volume less expensive than mixed nitrating acid, A. Cocking takes advantage of this fact[4] in an attempt to reduce the cost of operating the displacement process. The pertinent points in his patent are to run in sulfuric acid containing about 2% nitric acid onto the nitrated cotton as soon as the nitrating acid has been drained off, no water being admitted. After the sulfuric acid has uniformly saturated the nitrated cotton, it is gradually replaced by water as in the original process, a larger volume of more concentrated spent acid being thereby obtained.

The method is shown in Fig. 175, a charge of cotton, preferably thoroughly disintegrated is placed on the false bottom *b* of the vessel *a*, which contains the nitrating acid. After some hours, sulfuric acid containing 2% HNO_3 is run in at the funnel *d*, and the nitrating acid removed at the tap *e*. The nitrocellulose is preferably put under considerable pressure by means of the plate *c*, during the displacement of the nitrating acids. When the latter has been displaced the tap *e* is closed, water is run into the plate *c* through the central pipe *f*, the sulfuric acid being drawn off at the cock *g* at the same rate as the water enters, and part can be again used. The nitrocellulose is finally heated with water to boiling, but the residual acid may be first neutralized by a weak alkaline solution. In a modification of this process, the nitrocellulose after displacement of the nitrating acid, is treated in a centrifugal.

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[1] Zts. Schiess. Spreng. 1913, **8,** 119; abst. C. A. 1913, **7,** 1974.

[2] Arms and Explos. 1913, **21,** 37; abst. C. A. 1913, **7,** 1610. See also Courtois-Suffit, Mem. poud. salp. 1912, **16,** 87.

[3] D. R. P. 200292, 1906; abst. Zts. ang. Chem. 1908, **21,** 1854; J. S. C. I. 1908, **27,** 961; Mon. Sci. 1911, **75,** 93; Chem. Zentr. 1908, **79,** II, 559; Chem. Ztg. Rep. 1908, **32,** 445; Wag. Jahr. 1908, **53,** I, 432; Zts. Schiess. Spreng. 1908, **3,** 335.

[4] E. P. 16676, 1906; abst. J. S C. I. 1907, **26,** 717; C. A. 1908, **2,** 2181, 2197.

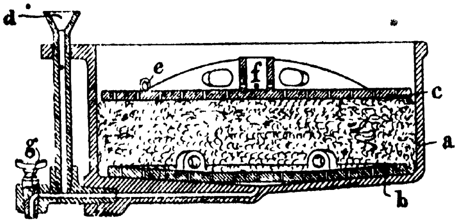

FIG. 175.—COCKING METHOD OF ACID DISPLACEMENT

It has long been known that the air in the cotton filament canal offers a certain appreciable resistance to the penetration of the acid, and it has been reasoned that removal of that air from the individual fibers would result in a more uniform nitration and more stable ester. The mechanics of this reason has been embodied in a recent patent, where the nitrating vessel is cylindrical in form and provided with an air-tight cover. Two acid reservoirs which can be either evacuated or placed under pressure are connected with the nitrating vessel. The pipe from one enters the bottom of the nitrating vessel, passes up the center, and delivers its acid at the bottom of the vessel just beneath a perforated false bottom. The cotton having been placed in the vessel, air is withdrawn from it by evacuating one of the acid reservoirs. The cock communicating with the other reservoir is then opened, the acid flows into the evacuated nitrating vessel, and is allowed to continue when the cock is closed and the acid which has been in contact with the cellulose sucked off into the other reservoir. This process is alternately repeated, the advantages claimed being that a very much more uniform nitration of the cellulose is thus obtained, and without additional labor.

J. Arnott[1] has described a means for effecting the distribution of separate delivery of liquids according to their varying specific gravities, in consequence which the liquid when of greater specific gravity is caused to act upon a float so as to keep the passage open through which liquid is to pass, but when the liquid is of the lower sp. gr. it will not sustain the float which then closes the passage, and the liquid of lower sp. gr. flows through the opening provided for it.

The apparatus has been more especially designed to allow spent acid from the manufacture of nitrocellulose by the Thomson process to run off from the nitrating pan into the waste acid main, and when the sp. gr. of the spent acid has reached a desired point, to automatically divert the acid to the waste water drain pipe. The waste acid after passing to the outlet cock enters a box at the bottom, at the top of which box a pipe leads out horizontally, at the end of which is a vertical down pipe terminating over the opening to the acid main, as shown in Fig. 119. Opening out through the bottom of the branch pipe *B* is a run-off tube, *D*, extending up beyond the opening *e* in the acid main *E*.

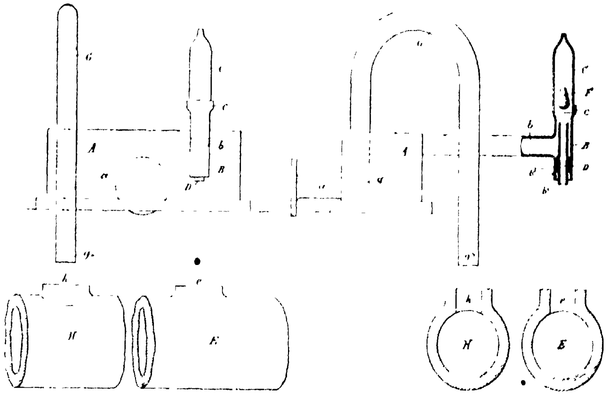

Fig. 176—Arnott Acid Distribution System

The operation of the process is as follows: On opening the outlet cock from the nitrating pans, the strong acid flows into the box *A*, and, when this has reached a sufficient height, acid will flow along the pipe *b* and will cause the float *F* to rise from off the top of the run-off tube *D*, and will (as long as the sp. gr. of the acid is sufficiently high) buoy up the float, thus enabling the acid to pass through the tube *D*, into the acid main *E*, through the opening *c*. As the liquid does not rise in the sight glass *C* to the level of the bend of the siphon *G*, the latter does not act and hence no liquid then passes through it.

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[1] E. P. 126375, 1919; abst J. S. C. I. 1919, **38**, 488-A.

When however, the sp. gr. of the liquid has fallen to a degree at which it will not run into the acid main *E*, but will run into the waste pipe *H*, the float *F* sinks and closes the top of the run-off tube *D*. The level of the acid then rises in the sight glass *C*, and in the siphon *G*, until the latter operates, which it continues to do until the liquid is drawn from the box *A*, and the nitrating pans are drained. As the level of the liquid of lesser sp. gr. in *A* should preferably be reduced below *b* as quickly as possible to prevent escape from the sight glass *C*, then *G* should be of sufficiently large bore to effect this.

In the method of E. Callenberg[1] the water replaces the nitrating acid gradually by displacement. The process is especially applicable for the manufacture of nitrocellulose filtering cloths, the latter, in pairs, being separated from each other during the acid removal washing process, by means of plates of an acid resisting material (aluminium). This facilitates the nitration, and also the subsequent washing without disintegration.

The Dupont Mechanical System of Cotton Nitration.[2] This method, developed at the du Pont plant at Haskell, New Jersey, has been widely used in the United States during the war for the nitration of cotton especially for military purposes. This is a three-floor system in which the nitration is carried on in pots, the material of which is then poured into centrifugals from which the acid is run. The arrangement is shown in Figs 177-181.[3] The dippers are located on the upper floor and the

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[1] D. R. P. 191656; abst. Wag. Jahr. 1907, **53**, II, 430; Chem. Centr. 1908, **79**, I, 182.

[2] Acknowledgment is made to the courtesy of E. I. du Pont de Nemours & Co. and to R. G. Woodbridge, Jr., chief of the Chemical Department for data and photographs in connection with this topic.

[3] Fig. 177. Interior Nitrating House, dipping floor partly dismantled

the cellulose is thus obtained, and without additional labor.

J. Arnott[1] has described a means for effecting the distribution of separate delivery of liquids according to their varying specific gravities, in consequence which the liquid when of greater specific gravity is caused to act upon a float so as to keep the passage open through which liquid is to pass, but when the liquid is of the lower sp. gr. it will not sustain the float which then closes the passage, and the liquid of lower sp. gr. flows through the opening provided for it.

The apparatus has been more especially designed to allow spent acid from the manufacture of nitrocellulose by the Thomson process to run off from the nitrating pan into the waste acid main, and when the sp. gr. of the spent acid has reached a desired point, to automatically divert the acid to the waste water drain pipe. The waste acid after passing to the outlet cock enters a box at the bottom, at the top of which box a pipe leads out horizontally, at the end of which is a vertical down pipe terminating over the opening to the acid main, as shown in Fig. 119. Opening out through the bottom of the branch pipe *B* is a run-off tube, *D*, extending up beyond the opening *e* in the acid main *E*.

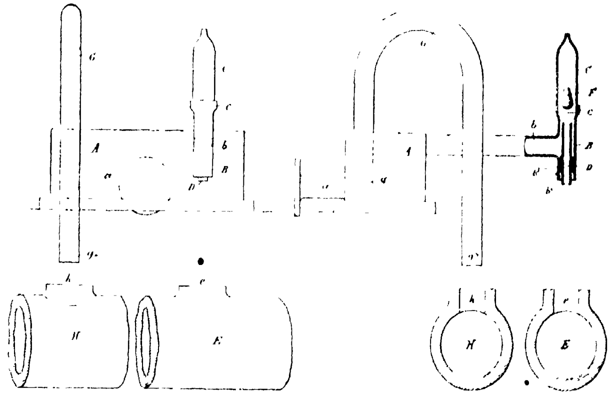

FIG. 176—ARNOTT ACID DISTRIBUTION SYSTEM

The operation of the process is as follows: On opening the

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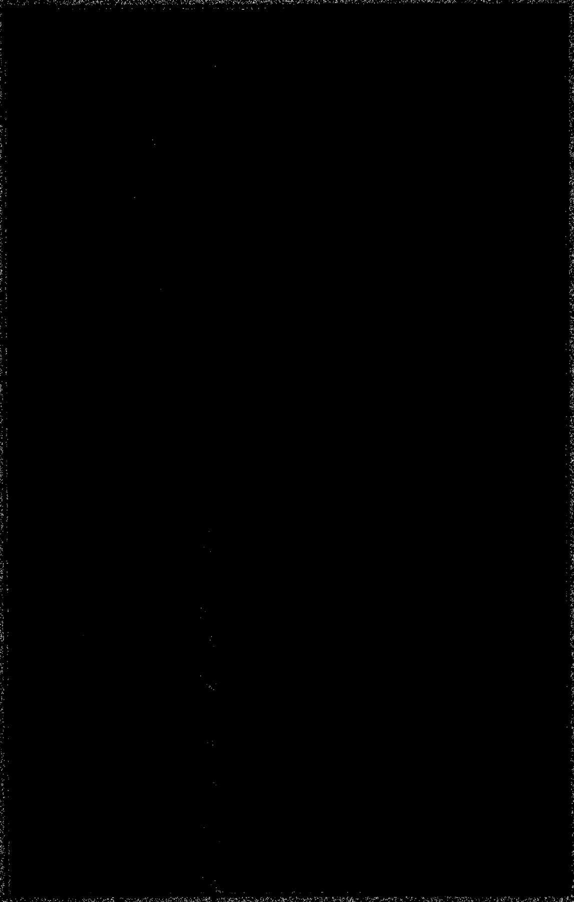
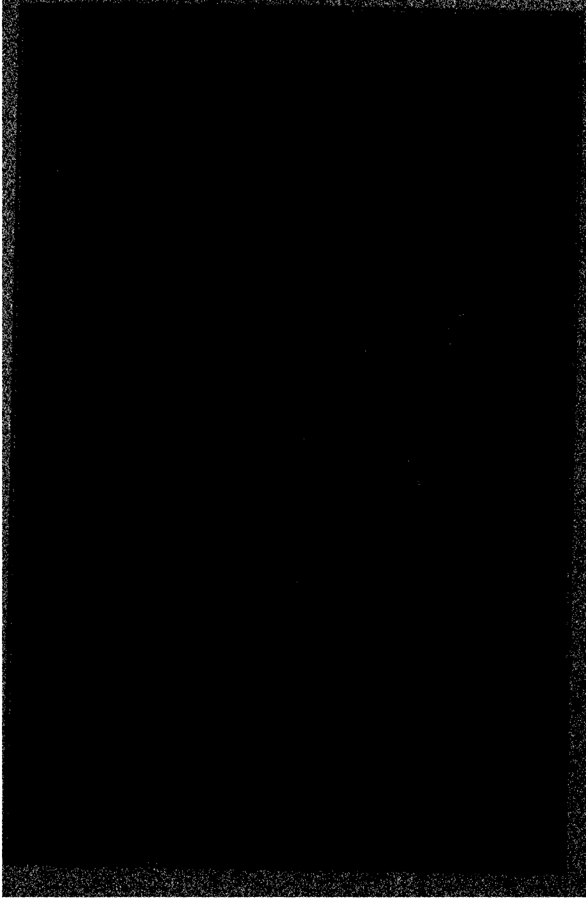
[1] E. P. 126375, 1919; abst J. S. C. I. 1919, **38**, 488-A.





[illegible]

the present time, the following description applies in particular to the nitration of cotton for pyronitrocellulose for use in military smokeless powders, and may be considered as typical.

The mixed acids are prepared for use in a Mix and Weigh House containing several scales and spent accumulation tanks. The spent acid is usually pumped into the scale tanks direct from the nitrating house, the accumulation tanks being used for storage of any excess of spent acid over that required to prepare the mixes. The spent acid is fortified by adding the proper calculated weights of fuming sulfuric acid and a mixed acid high in nitric. The mix is then agitated, sampled, and if found satisfactory by analysis is run through the warming house tanks, where the acid is brought to the proper temperature by means

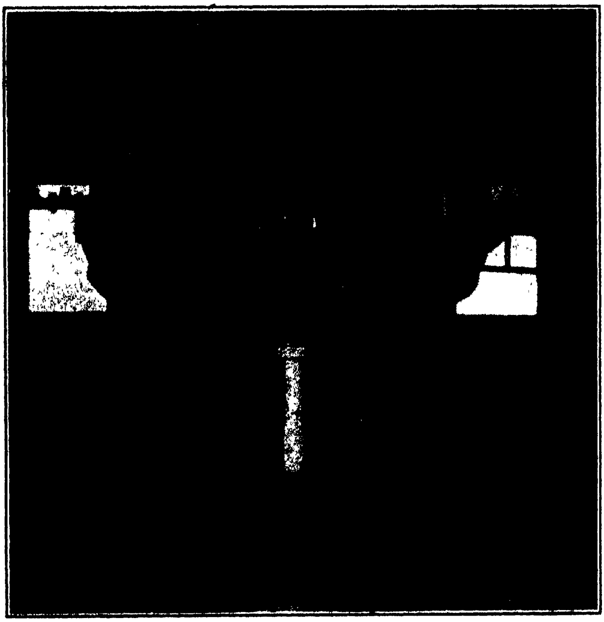


FIG. 179.—DuPONT MECHANICAL COTTON NITRATION

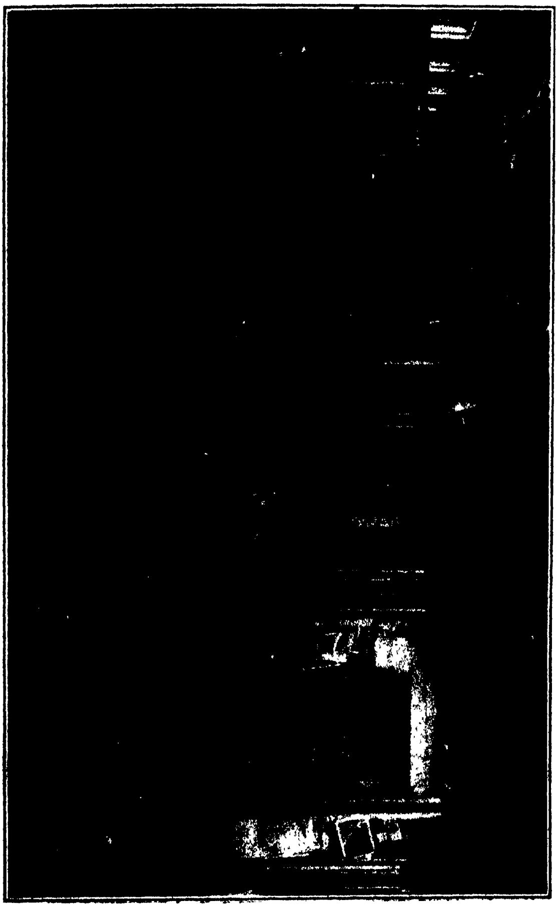


Fig. 180.—Nitrating House, Dipper Floor

of steam or water in coils inside the tank or running water on the outside. From the warming house the acid is pumped to the measuring tanks on the dipper floor of the nitrating house.

A standard nitrating house contains 9 units consisting of a total of 36 mechanical dippers and 9 centrifugal wringers. On the third or monitor floor are the motors driving the wringers.

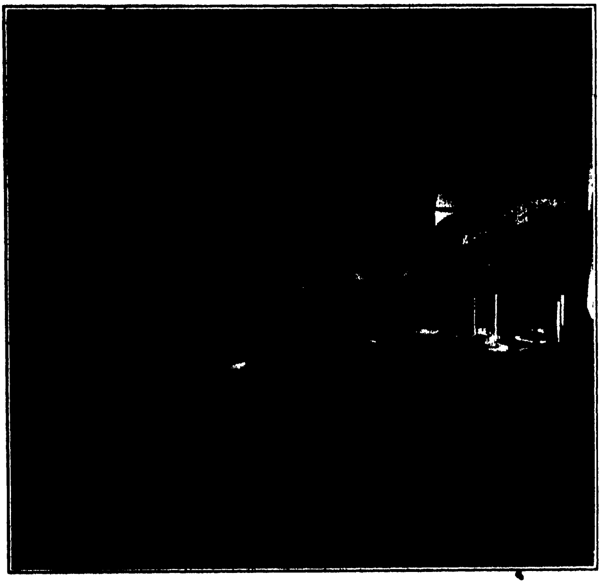


FIG. 181.—DUPONT MECHANICAL COTTON NITRATION

The dippers and measuring tanks are located on the second floor, one measuring tank to each unit of 4 pots. The wringers are on the ground floor, and the drowning basins, fume lines, etc., are located in the basement. The dry cotton is received on the dipper floor from the dry house in cans on a telpherage car. About 35 lbs. constitute a dipper charge, with about 1500 lbs. mixed acid. In dipping a charge the fume line from the top of the pot is opened, the agitators started, and about one-third of the acid run in. A more uniform wetting of the cotton results.

The cotton is then added while the acid continues to run in. Care is taken to break up any lumps of cotton, and the flow of acid is controlled so that the cotton is charged before all the acid is in. After 25 minutes, nitration is considered complete and the charge is dropped through the Universal adapter line into the wringer. The wringers are 42" in diameter and perforated. A valve plate which fits around the wringer shaft is used to close the opening in the base of the basket through which the nitrocellulose is discharged. To protect the operator from acid spattering while charging the wringer, and to maintain suction and prevent foreign material from getting into the wringer during the operation, there is provided two aluminium covers over the wringer top. In charging, the machine is run on low speed, the pot valve on the 6" adapter line opened, and the charge run into the basket. The valve is then closed, the wringer put on high speed, and the charge run for $3^1/_2$ minutes. The power is then shut off, the valve plate is raised, and the charge forked down into the drowning basin, where it is submerged in water and carried by gravity to the pump house, from which it is pumped to the boiling tub house.

The spent acid flows by gravity from the wringers through filters to remove any nitrocellulose and then to the storage tanks, from which it is pumped to the Mix and Weigh House. The same acid is used as for the regular centrifugal method of nitration, and the same proportion of acid to cotton, i. e., 50 to 1, breaks up the cotton uniformly and tends to maintain a uniform temperature during the nitration period. The nitration in general gives a product a few hundredths of a per cent. higher in nitrogen than the regular centrifugal method and, under the same acid conditions, this would seem to indicate a more thorough nitration with less unnitrated cotton.

A. du Pont and J. Thompson,[1] have described an apparatus for nitrating cellulose, comprizing a rotating platform, a plurality of equi-spaced nitrating vessels each having a perforated false bottom and pivotally mounted around the circumference of the platform, a valve-controlled outlet from the lower portion of each vessel and fixed devices to open and close the valves at different points in the rotation of the platform, an acid measuring receptacle being centrally mounted on the platform and supplying acid to the nitrating vessels successively. In the N. Kaltenbach process,[1] for the construction of cellulose nitrating chambers, the several swinging nitrating pots are arranged in a chamber provided with control and working towers, which have only upper and lower openings for the entrance, all acid in the air is blown into the working chamber, so that the nitrous fumes are constantly drawn off by this air current and cannot reach the working man upon opening the tower. A car within the chamber empties the nitrated cellulose and carries it to the centrifuge from which the material is delivered into the working chamber by hydraulic action. In the G. Fussell system,[2] the apparatus comprizes a casing with the continuous acid-receiving gutter at its bottom, a perforated basket rotatably mounted in the casing above the acid receiving gutter, and spaced a slight distance away from the walls of the casing, and a rotatably mounted hollow screw within the basket. One edge of the screw below the thread is cut away to form an opening for the passage of the cotton which is then sent upwards by the action of the screw. In another recent arrangement for centrifugal nitration of cotton, the above centrifugal is affixed to iron rollers tilted so as to drain into the wringer. After centrifugal wringing, the nitrocotton is put through these rollers which squeeze out an additional amount of acid. By separating in this manner, the acid in the nitrating cotton will, in some instances, be reduced to as low as 20%. In the nitrocellulose centrifugal separator of F. Mataousek[3] and shown in Fig. 182, the material to be separated, e. g., a mixture of nitrocellulose and nitrating acid, is fed from the rotating hopper *20*, through the corrugated outlet, *22*, which can be closed more or less by the corrugated cone *26*, into the bowl *16*, which is provided with a perforated spiral corrugation *19*. The liquid is discharged through the perforations into the inner casing *2*, and the solid portion is discharged over the lip of the bowl *16*, into the annular space between the casings *1* and *2*. Means are provided for flooding or flushing out both the feed hopper and the bowl with water.

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[1] U. S. P. 979560, 1910; abst. C. A. 1911, **5**, 993; Mon. Sci. 1911, **75**, 107; Chem. Ztg. Rep. 1911, **35**, 159.

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[1] F. P. 453588, 1913; abst. C. A. 1914, **8**, 251; J. S. C. I. 1913, **32**, 768; Chem. Ztg. 1913, **37**, 557; Chem. Ztg. Rep. 1913, **37**, 572; Kunst. 1913, **3**, 416.

[2] U. S. P. 1296280, 1919; abst. C. A. 1919, **13**, 1533; J. S. C. I. 1919, **38**, 390-A.

[3] E. P. 118262, 1918; abst. J. S. C. I. 1918, **37**, 637-A.

Other Nitration Methods. H. Diamanti, H. Champin and P. Loisif, have patented a process for the manufacture of nitrocellulose whereby the acids are either partially or completely renewed during the process of nitration, continuous circulation being also employed. The process is said to be applicable to nitrating vessels of all descriptions, and the composition and temperature of the mixed acid is thus kept constant.[1]

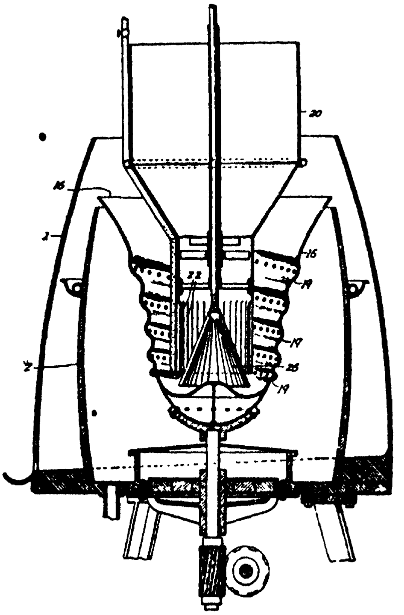

FIG. 182.—THE F. MATOUSEK NITRATING CENTRIFUGAL

An improvement on this apparatus has been devized which consists of a battery of nitrating vessels placed in a polygonal-shaped chamber and intended especially for carrying out the process described above.[1] The method is illustrated in the accompanying figure (183), which are sections of one of

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[1] F. P. 377425, 1906; abst. J. S. C. I. 1907, **26**, 1066. For the discussion of the kinetics of nitration consult H. Martinsen, Zts. physik. Chem. 1904, **50**, 385; 1907, **59**, 605; abst. Chem. Centr. 1905, **76**, I, 438; 1907, **78**, II, 1496; J. S. C. I. 1908, **27**, 139. The G. Simpson formula for the nitration

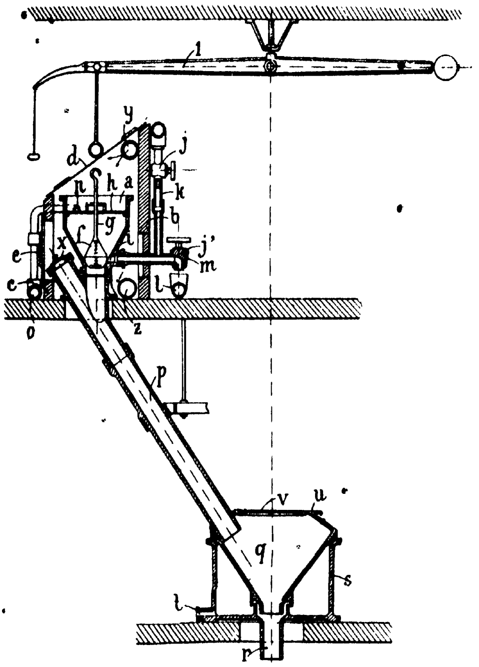

FIG. 183.—DIAMANTI METHOD OF COTTON NITRATION

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of photographic collodions is given in Year Book Pharm. 1870, 31. Soc. Anon. de fabrication de dynamite, F. P. 127843, 1878; abst. Mon. Sci. 1879, **21,** 1047. D. R P. 201623, 228544; abst. C. A. 1911, **5,** 2011; Chem. Zentr. 1908, **79,** II, 1218, 1910, **81,** II, 1693; Chem. Ztg Rep. 1908, **32,** 574; 1910, **34,** 615; Chem Zts. 1909, **8,** 1133; Jahr. Chem. 1905–8, II, 1506; 1910, **63,** I, 416; Wag. Jahr. 1908, **54,** II, 26; 1910, **56,** I, 626, Zts. ang. Chem. 1908, **21,** 2476; Zts. Schiess. Spreng 1908, **3,** 395.

[1] F. P. 379509, 1906; abst. J. S. C. I. 1907, **26,** 1256. The C Mitchell process of cotton nitration (Amer. J. Pharm. (4), **2,** 241; abst. Bull. Soc. Chim. 1872, **18,** 373; Mon. Sci. 1874, **16,** 382; Poly. Notiz. 1873, **28,** 96; Phot. Archiv. 1873, 12; Poly. Centr. 1873, **39,** 593; Elsner Mitth. 1872–3, **22,** 49; Pharm. Trans. (3), **2,** 1047; Chem. Centr. 1872, **43,** 554; Jahr. Chem. 1872, **25,** 984. See also Zts. allg. oester. Apotheker-Vereins, 1875; abst. Indbl. 1876, 235; Chem. Tech. Rep. 1875, **14,** II, 217) is adapted to the pro-

the nitrating vessels and its accessories. The nitrating vessel *A*, of earthenware, is closed at its lower end by a plug *F*, provided with a long handle terminating in a hook. The nitrating acid enters the pot through the opening *I*, by turning the cock *J*. A glass tube, *K*, allows the rate of flow to be observed. The vessel can, if necessary, be emptied by turning the cock *J'*. The vessel being filled to the required level with acid, a charge of cellulose is introduced through *D* and kept pressed down by the perforated plate *H*. When nitration is complete the cock *J* is turned and the spent acid displaced by fresh acid and forced through the opening *N*, into the tube *O*, leading to the acid reservoir. The strong displacing acid is then shut off and the plug *F*, raised by means of a lever; the acid and nitrocellulose passing by the inclined pipe *P*, to a perforated funnel. The bulk of the acid flows through the perforations and away to the acid storage tanks, while the nitrocellulose, with adherent acid, passes through the stem of the funnel to the centrifugal machines. A current of air at any desired temperature can be introduced into the compartment containing the nitrating vessel by the opening *Y* and discharged at the exit *Z*.

According to patents issued in various countries to G. de Briailles, nitrocellulose may be produced by electrolyzing a mixture of concentrated sulfuric acid and strong nitric acid in the presence of cellulose.[1] The acids are stated to be thus electrolytically concentrated. The glass vessel, shown in 184 has a glass valve, *9*, a porcelain shelf, *12*, with cellulose on top of it, platinum or gilded platinum electrodes, *16* and *17*, a thermometer, *14*, and a micrometer in a vertical perforated glass

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duction of a perfectly soluble pyroxylin for photographic use The Nichol process (Phot News, Jan 1862; abst Rep Chim Appl 1862, **4,** 117; Pharm J Trans. **2,** 458) is similar

[1] E. P. 2902, 1906, abst J S C I 1907, **26,** 114, C. A 1907, **1,** 925. Belg P. 189782, 1906 D R P 203377, 1906, abst Jahr Chem. 1905–8, 974; Wag Jahr 1908, **1,** 430, Zts. ang Chem 1908, **21,** 2367, Chem Zentr. 1908, II, 1843; Chem Tech Rep 1908, **32,** 651, Chem Ind 1908, **31,** 716; C. A 1909, **2,** 718. F. P. 364349, 1906, abst C. A. 1907, **1,** 2326, J. S. C. I. 1906, **25,** 911. U.S. P 874564, 1907; abst. J S C. I 1908, **27,** 92 For the action of acetyl nitrate as a nitrating agent (made by the action of nitric anhydride on acetic anhydride), see A. Pictet, D. R. P. 200201, 1907; abst. J. S. C. I. 1908, **27,** 988; Chem. Zentr. 1908, **79,** II, 552; Chem Ztg. Rep. 1908, **32,** 434; Jahr Chem 1905–8, II, 359; Wag. Jahr 1908, **54,** II, 15; Zts. ang Chem. 1908, **21,** 2103, Zts Schiess. Spreng. 1908, **3,** 334; Friedlaender, **9,** 70. A. Stettbacher, Die Seife, 1919, **3,** 609, abst Chim Ind. 1920, **3,** 219.

cylinder. The anode *16* is close to the porcelain shelf. The immersed cellulose is nitrated in from three to four hours, but the temperature must lie between the limits 30° to 40°. The nitrous acid necessarily produced at the cathode is stated to assist in the nitration of the cellulose. It is claimed the same mixture of acids can be used for an indefinite length of time, except that part of the nitric acid which combines to form nitrocellulose. Washing is effected by removing the acid pipe and acid suction pump, and further, the cellulose can be squeezed by means of the porcelain piston *18* passing through the flexible India rubber stopper *19*. Water is then fed into the apparatus through the tube *8* and then withdrawn. The receptacle is then opened and the nitrocellulose further washed in the air. Before nitration of the next lot of cellulose the moisture left in the vessel is carefully removed by pumping. It is claimed for this method that the degree of nitration may be readily controlled by operating under constant conditions of concentration of acid, temperature of reaction, and time of nitration, this constancy being maintained by passing through the reacting solution an electric current of three to four volts, whereby the water formed in the reaction is decomposed and the liberation of heat which would accompany the dilution of the acid thereby prevented.

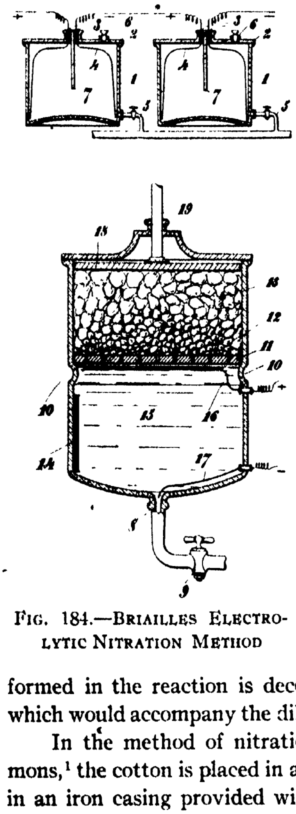

FIG. 184.—BRIAILLES ELECTROLYTIC NITRATION METHOD

In the method of nitration *in vacuo* as outlined by L. Dumons,[1] the cotton is placed in a perforated basket which is enclosed in an iron casing provided with an aluminium lid. A pipe with a cock delivers the mixed acid for nitrating through the top of the casing, and a pipe provided with a cock leads from the bottom of the casing to a tank which can either be exhausted or placed under the pressure of compressed air. The upper cock being closed, the whole apparatus and the lower tank are exhausted. The cock on the acid supply pipe is then opened and a stream of acid flows through the cotton in the perforated basket and into the tank below, where it can be revivified, pumped up again into the upper supply tank and passed once more through the cotton. When nitration is completed, the perforated basket is removed to a centrifugal and the excess of acid expelled.

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[1] F. P. 445833, 1912; abst. J. S. C. I. 1912, **31**, 1203. E. P. 14003, 1913; abst. J. S. C. I. 1914, **33**, 222; C. A. 1914, **8**, 3860; Chem. Ztg. 1913, **37**, 968. Belg. P. 257404, 1913; abst. Chem. Ztg. 1913, **37**, 1026.

It is claimed that this process, in view of the exhaustion of air from the cotton fiber and the large quantity of mixed acid used, produces a more highly nitrated and uniform product than is obtained by the usual methods.

In an improvement of this process which admits of nitrating cotton *in vacuo*,[1] the bottom of the nitrating vessel is connected with a three-way cock by means of which it can be connected with one or other of two receivers. By means of a four-way cock, which is operated in unison with the three-way cock, each of these receivers can be connected alternately with a suction device and with a supply of compressed air. The nitrating acid flows from a high level reservoir into the nitrating vessel and thence into each of the low level receivers in turn, whence it is raised by the compressed air again to the high level reservoir.

In the preparation of nitrocellulose as described by the Vereinigte Kunstseidefabriken, A. G.,[2] and intended primarily

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[1] First add. dated Feb 14, 1914, to F. P. 445833; abst. J. S. C. I. 1915, **34**, 101.

[2] Vereinigte Kunstseidefabriken, A. G. and K. Schniter, F. P. 455011, 1913; abst. C. A. 1914, **8**, 424; J. S. C. I. 1913, **32**, 886; Kunst. 1913, **3**, 436; Chem. Ztg. Rep. 1913, **37**, 605. D. R. Anm. V-10703, 1912. U. S. P. 1093012, 1914; abst. C. A. 1914, **8**, 2062; J. S. C. I. 1914, **33**, 569. Swiss P. 63365, 1913. Belg. P. 254537; abst. Kunst. 1913, **3**, 355. E. P. 5553, 1913; abst. J. S. C. I. 1914, **33**, 161; C. A. 1914, **8**, 2949.

In the apparatus described in Fig. 185, *a* is a vessel provided with a removable lid, in which vessel the nitration takes place. An outflow pipe, *b*, is provided below leading to a pump *c*, from which a pipe *c'*, passes to discharge the

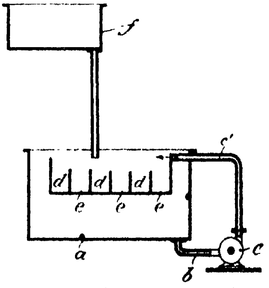

FIG. 185.—THE SCHNITER COTTON NITRATION PROCESS

to obviate or minimize the tendency of cotton during nitration to "fume off," or burn, the cellulose is nitrated in vessels with perforated bottoms, the acid being circulated by means of a pump. After nitration is complete the acid is allowed to drain off and the nitrated product washed with cold acid from a previous operation. When the nitrocellulose has thus been sufficiently cooled, the acid is separated and the treatment continued by the usual methods. The patentees claim that by this method of treatment spontaneous decomposition of the nitrocellulose is entirely eliminated, and the process apparently has distinct elements of merit.

In an uninterrupted process of cellulose nitration as devized by C. Crepelle-Fontaine,[1] the cellulose is charged into the nitrating fluid in a counter-current and simultaneous change of direction through a U-shaped canal, which includes in its vertical parts a container for the liquid in which transporting members always retain a horizontal position, and which carry the cellulose in such a manner that during its movement through the canal, first from the bottom upwards, then from the sides and lastly from the top downwards, a uniform nitration results.

With the idea in mind of producing a nitrocellulose more uniform in its character and qualities than any heretofore prepared, J. France[2] has been granted patent protection for a proc-

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liquid into the cells *d*, arranged within the vessel *a*, containing the material to be nitrated The bottoms *e* of these cells are perforated The apparatus is resistant to acid and does not allow the acid to escape When the pump *c* is started the acid from the vessel *a* is forced by the pump through the pipe *c'*, on to the cotton in the cells, penetrates therethrough and runs back into the vessel *a*, through the perforated bottoms *e*, the circulation of acid being continued while the pump is in operation When the nitration is completed, the pump *c* is shut off and the acid in the cells *d* is allowed to run off. As soon as this is done, the cooled acid from an earlier operation is allowed to drop from a second container, *F*, over the nitrated material until the latter has been sufficiently cooled. The material is then centrifugalized from the acid and further treated in the usual manner

[1] D. R P. 239163, 1910; abst. C. A. 1912, **6,** 2169; Wag. Jahr. 1911, **57,** I, 477; Zts. ang. Chem. 1911, **24,** 2281; Chem. Ztg. Rep. 1911, **35,** 596; Zts Schiess. Spreng 1911, **6,** 474 D. R P. Application C-19173, 1910 F. P. 397707, 1908; abst. Chem. Ztg. 1909, **33,** 341. See J Bernadou, F P. 307918, 1901; abst. Mon. Sci. 1902, **58,** 158.

[2] E. P. 17692, 1888; 20964, 1889; 5364, 1890; abst. J. S. C. I. 1889, **8,** 160, 303; 1890, **9,** 821. U. S. P. 420445, 420446, 420447, 1890; abst. J. A. C. S. 1890, **12,** 22. D R. P. 50921; abst. Chem. Tech. Rep. 1890, **29,** I, 113; Ind. Bl. 1890, 294; Ber. 1890, **23,** 475; Chem. Centr. 1890, **61,** II, 31, Tech. Chem. Jahr. 1890, **13,** 154, Wag. Jahr. 1890, **36,** 1178

ess whereby ordinary raw cotton, in which the natural impurities have not been removed, is finely comminuted and in this condition directly introduced into the nitrating bath. Before nitrating the product is repeatedly washed, but not with the addition of alkali or other material intended to emulsify the natural wax of the cotton. Fig. 186 shows a side elevation of the machine designed to cut up this cotton. The natural cotton is fed along an endless band, *N*, through rollers *R* and *R'*, and over a knife, *K*. The cotton is held over the knife by pivoted clamps *C'*, which receive a reciprocating motion from a cam on the shaft *S''*, the same motion also actuates the pawls of the feed ratchet wheel *R''*. The knives *K* are mounted on a wheel *W*, driven by the spur wheel *G*. It was found, however, that the homogeneous, dust-like, mechanically comminuted cotton fiber, although nitrating readily and uniformly, was in such a fine state of subdivision that the yield was not only materially reduced, but the spent acid contained so much cotton in solution and in suspension that the process commercially was not feasible.

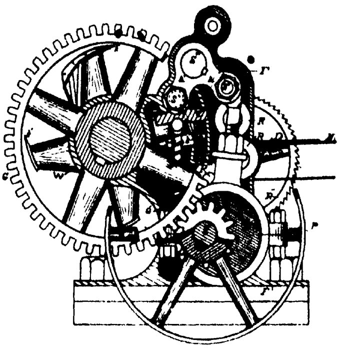

Fig. 186.—France Method of Cotton Comminution

The process of S. Mackie,[1] Fig. 187, is somewhat similar to that of France, in that the cotton is treated with acid to convert it into guncotton in the tank *c*, the cotton pulp being delivered from the hopper *a* by spiked roller *b*, the acid entering through the pipe *d*. This causes the cotton to fall on to the grating *e*, where it is immersed by the wheel *f*, propelling it towards the outlet *g*, from which outlet the material is fed into digesting pots in the usual manner, a number of which, for convenience, are mounted in a cradle so that they can be transported

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P. Berard (E. P. 1883, 1857. F. P. 18267; abst. Mon. Sci. 1868, 1041; Wag. Jahr. 1868, **14**, 358) was the first to powder cotton for facility of nitration.

[1] E P 445, 1873; abst. Chem. News, 1873, **28**, 192.

by an overhead crane to the cooling department. The cotton is freed from acid in the usual manner by a hydro-extractor or by pressing rollers, after which it is washed.

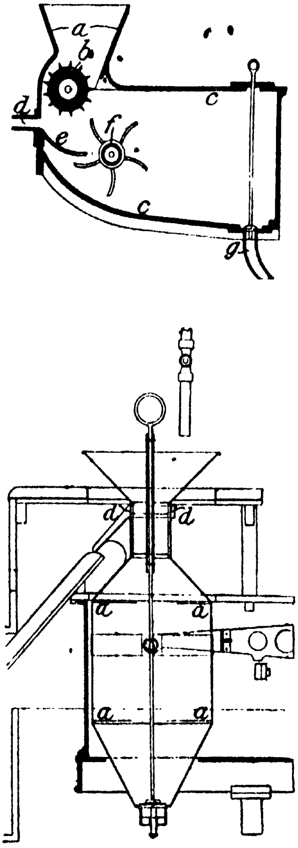

Fig. 187.—Mackie's Process for Cotton Nitration

G. Wolf[1] recommends the following process for the preparation of a pyroxylin which is said to yield with ether-alcohol a perfectly clear and colorless solution: 20 parts of crystallized potassium nitrate are triturated in a mortar; 36 parts of sulfuric acid of specific gravity 1.84 are added, and when the mixture has cooled, one part of cotton is incorporated in such a manner that the latter will be uniformly impregnated. After ten minutes the nitrated cotton is placed in a laterally perforated funnel, which is dipped in water and washed until the latter ceases to acquire an acid reaction. This is somewhat similar to the method of J. Bienert,[2] who operates with a mixture of six parts of sulfuric acid of specific gravity 1.84 and three parts of nitric acid of specific gravity 1.41 to 1.42, and when the mixture has cooled to between 20° to 25°, one part of cotton is introduced, which is thoroughly stirred and set away at room temperature for a period of 24 hours. The end of the nitration period is indicated by the change of the parchment-like appearance of the cotton and by its becoming soft again, but it is advisable to ascertain its solubility before the final washing process takes place.

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[1] Proc. Am. Phar. Assoc. 1883, **31**, 242; Amer. J. Pharm. 1883, 273; Pharm. Zts. Russl. 1883, **22**, 4; Jahr. Chem. 1883, **36**, 1779.

[2] Zts. Pharm. **22**, 4; abst. Jahr. Chem. 1883, **36**, 1779. Product called colloxylin.

It is evident that these two processes are primarily intended for the manufacture of pharmaceutical collodions in small amounts, and where the element of cost is not the predominating factor.

W. Godeffray has determined that collodion cotton which is rapidly and perfectly soluble may be obtained by immersing 35 parts of absorbent cotton previously deprived of fat by heating with a solution of sodium carbonate, the cotton being introduced into a mixture of 700 parts sulfuric acid and 350 parts of dry potassium nitrate at 56° for a period of seven minutes. The nitrated product is then transferred to a large container filled with hot water and finally thoroughly washed in a current of cold water until the acid is completely removed. It is claimed that longer exposure to the nitrating mixture does not deleteriously influence the quality of the collodion cotton, but it is also evident that continued immersion in the acid mixture at this high temperature must result in a increase in fluidity and in solubility of the final nitrated product.[1]

A patent has been granted to A. Viswinkel for a process for the direct manufacture of gelatinized nitrocellulose in which ordinary fat-free, dry cellulose is treated with a mixture of equal parts zinc chloride solution, acetic acid and fuming nitric acid at a temperature of 10° to 15°. According to the patent description, the mass gelatinizes within a few days and can be readily washed from acid to a neutral condition.

It is evident that a cotton nitrated in this manner must have a low stability and a fluctuating solubility and viscosity.[2]

The Patronenfabrik, Saxonia, have received patent protection in Germany and in England for a process of nitrocellulose, nitrohydrocellulose and nitrooxycellulose manufacture which is characterized by a treatment of cellulose with concentrated sulfuric acid at a low temperature until the morphological structure of the cotton has entirely disappeared, when nitration is carried on with about the theoretical quantity of nitric acid.[1]

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[1] Proc. Am. Pharm. Assoc. 1877, **25**, 285; Zts. Oesterr. Apoth. Ver. 1877, 709; abst. Year Book Pharm. 1877, 241; Poly. Notiz. 1877, **32**, 167. In the T. Best process (E. P. 15121, 1884; abst. Wag. Jahr. 1885, **31**, 1149; 1886, **32**, 1004; J. S. C. I. 1885, **4**, 751) cellulose, after treatment with nitric and sulfuric acids, is bleached by saturation with SO_2 at 100° F. in a closed vessel.

[2] D. R. P. 74070; abst. Jahr. Chem. 1894, 1134; J. S. C. I. 1894, **13**, 1134; Wag. Jahr. 1894, 495; Zts. ang. Chem. 1894, **7**, 307; Chem. Centr. 1894, **65**, I, 1168; Chem. Ztg. 1894, **18**, 612, 1090; Chem. Tech. Rep. 1894, **18**, I, 239; Chem. Ind. 1894, **17**, 512; Ber. 1894, **27**, R, 537; Tech. Chem. Jahr. 1893–4, **16**, 165.

In a subsequent application,[2] attention is called to the fact that in the usual process of cotton nitration by immersing cotton fibers free from fat in a mixture of nitric and sulfuric acids and subsequent removal of the acid by long boiling, washing and pulping, the nitrocellulose obtained as a result of the process retains the structure of the crude fiber. On the assumption that this nitration process is irrational and complicated, and a long and tedious operation, especially true as regards the comminution or pulping process, repeated efforts have been made to simplify and, if possible, to unite the two operations into one. It has especially been tried to carry out the comminution operation before nitration, as in the patented process of J. France, on the assumption that a higher nitrated product of greater uniformity of composition would thereby be obtained.

In the process of this application the above enumerated drawbacks are claimed to be substantially eliminated, as the pulping and nitration operations are carried out simultaneously and the nitration of pulverulent material is thereby avoided.

The process as described is carried out in the following manner:

The crude material is placed in concentrated sulfuric acid and stirred up to a paste or semi-solution. The nitration is carried out with the theoretical amount of nitric acid, or an amount slightly in excess of the theory. The quality of the finished product is influenced and the yield is guided by a variation of the temperature and concentration of the reacting acids. By modifying both of these conditions, higher or lower nitrated products may be obtained which are soluble or insoluble in ether or alcohol, or mixtures of them, depending upon the amount of nitrogen which is introduced into the cellulose molecule. The addition of the sulfuric acid to the cotton takes place at a low temperature, the nitric acid being added, with cooling, after the cotton structure has apparently been entirely destroyed. The nitro product is then precipitated by means of a large amount of cold water, pressed or centrifugalized and washed to neutrality.

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[1] Belg. 175773, 1904. E. P. 5126, 1904; abst. J. S C I. 1904, **33,** 560; Chem. Ztg. 1905, **29,** 751 F. P. 340527, 1904; abst. J. S. C. I. 1904, **33,** 837; Chem. Zts 1904, **3,** 621, Mon. Sci. 1905, **63,** 86. U. S P. 860776, 1907; abst J. S C. I. 1907, **26,** 991; C A. 1907, **1,** 3064; Mon. Sci. 1908, **69,** 60; Zts. Schiess Spreng. 1908, **3,** 18; Chem. Ztg. Rep 1907, **31,** 474. D. R. P. Appl V-4865. D R. P 198284, 1903; abst. Chem. Centr. 1908, **79,** I, 1912; J. S. C. I. 1908, **27,** 837, Mon. Sci. 1911, **75,** 63; Chem. Ztg. Rep. 1908, **32,** 283; Jahr. Chem 1905-8, II, 973; Wag Jahr. 1908, **54,** I, 430; Zts. ang. Chem. 1908, **21,** 1661; Zts. Schiess. Spreng. 1908, **3,** 214.

[2] Patronenfabrik and A. Voigt, D R. P. Appl. 5358. D. R. P. 249272, 1907; abst C. A 1912, **6,** 3330; Zts. ang. Chem. 1912, **25,** 1878; Wag. Jahr. 1912, **58,** I, 428; Chem. Zentr. 1912, **83,** II, 402; Chem. Ztg. Rep. 1912, **36,** 494. U. S. P. 855869, 1907; abst. J. S. C. I. 1907, **26,** 780. U. S. P. 860776, 1907; abst. Mon. Sci. 1908, **69,** 60; Zts. Schiess. Spreng. 1908, **3,** 18; Chem. Ztg. Rep. 1907, **31,** 474; C. A. 1907, **1,** 3064. E. P. 3788, 1914. See also A. Voigt (E P. 5126, 1904; abst. Chem. Ztg. 1905, **29,** 751; J. S. C. I. 1904, **23,** 560) who nitrates cellulose by dissolving in sulfuric acid at 2-3°, concentrated nitric acid being then added.

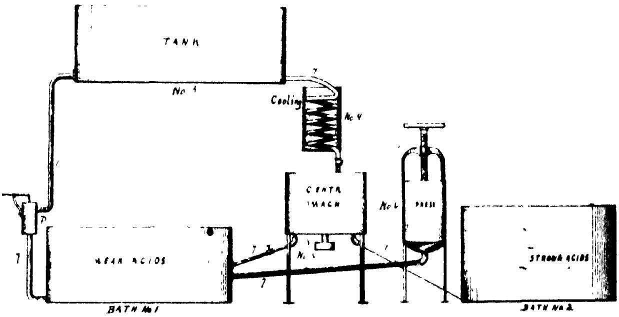

FIG. 188.—THE MAXIM PROCESS FOR COTTON NITRATION

In the English patent of O. Schmidt,[1] issued in 1904, is described a process of nitration in which granular cellulose is well soaked in concentrated nitric acid, which may or may not contain from one-fifth to one-fourth of its bulk of sulfuric acid, depending upon the properties desired in the final product. When the cellulose has swollen and become partially disintegrated, concentrated sulfuric acid is added, which brings about nitration and hardening (parchmentizing), and is then washed with water in the usual manner.[2]

Hudson Maxim assigned to the Columbia Powder Mfg. Co.

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[1] E. P. 116, 1904; abst. J. S. C. I. 1904, **23**, 385; Chem. Ztg. 1905, **29**, 514.

[2] This method is claimed as an improvement on that described in English specification No 4769 of 1895; abst. Chem. Centr. 1896, **67**, I, 1150; Chem. Ztg. 1896, **20**, 652; J. S. C. I. 1896, **15**, 68, 134.

of New York, in the year 1892,[1] *a method for guncotton manufacture in which the cellulose is first immersed for* a short time in a bath of strong nitrating acid and is then, with a large quantity of contained acids, fed to a second bath which contains an excess of weaker acids. It is there digested for a considerable time, the object being to increase the stability of the final product. The operation is afterwards finished in the usual manner.

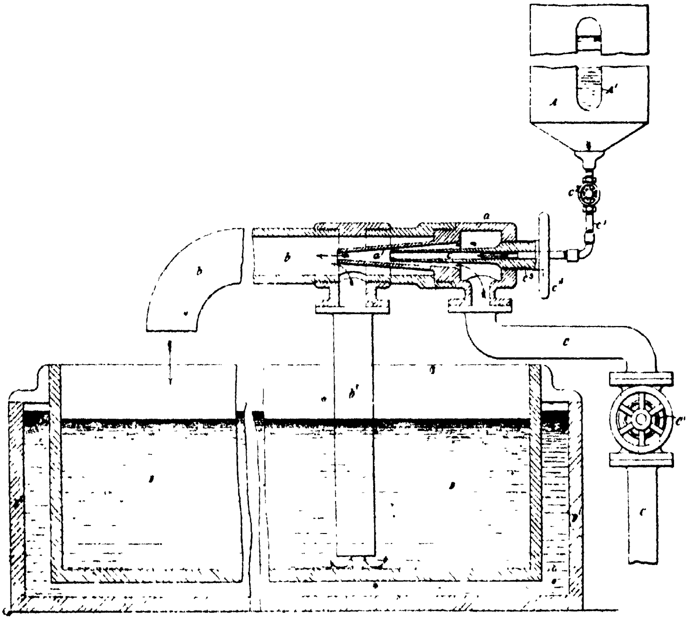

FIG. 189.—MAXIM COTTON NITRATION PROCESS

In order to obviate the necessity for gelatinizing guncotton when intended for smokeless powder use, A. Luck and A. Durnford[1] nitrate and gelatinize in one and the same process, obtaining a product in a dense, powdery form so that it can be finished, like ordinary black powder, by rolling or granulating. The original cellulose is dissolved in dilute sulfuric acid, aqueous zinc chloride, zinc chloride, hydrochloric acid or a mixture of caustic alkali, carbon bisulfide and water. The solution is agitated and by dilution or heating, the cellulose is re-precipitated in gelatinized granules. These are washed and dried with constant agitation, then run through a hopper into the mixed acids and are nitrated as usual.

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[1] U. S. P. 465280, 1891; abst. J. A. C. S. 1891, **13**, 304. U. S. P. 479988; abst. J. A. C. S. 1892, **14**, 295; Chem. Ztg. 1892, **16**, 1236; Tech. Chem. Jahr. 1892–3, **15**, 171. E. P. 5209, 1890; abst. J. S. C. I. 1890, **9**, 438; 1891, **10**, 292, 484. E. P. 15485, 1890; abst. J. S. C. I. 1891, **10**, 794; Chem. Tech. Rep. 1892, **31**, I, 224; Chem. Ztg. 1892, **16**, 424; Meyer Jahr. Chem. 1892, **2**, 363; Tech. Chem. Jahr. 1891–2, **14**, 138. E. P. 4129, 1891; abst. J. S. C. I. 1892, **11**, 199, 456; Chem. Tech. Rep. 1892, **31**, I, 224; 1895, **34**, I, 214.

It must be said of this process that guncotton prepared in this manner invariably has a low stability and therefore is of but little value for smokeless powder uses.

In order to prepare guncotton or collodion cotton in a quick, effective and continuous manner, J. Beck and O. Nenninger,[2] have described an apparatus (Fig. 190) which comprizes an exterior casing, an interior U-shaped acid tank, an endless chain passing through the tank, formed of linked plates having teeth for feeding the cotton to the acid in the tank; means for heating the tank, and a rotating tooth roller which is located at the outgoing end of the tank and adapted to remove the nitrated cotton from the links of the chain. The absorbent and partially bleached cotton is fed into the acid in the tank *B*, and by the uniform immersion of the cotton in the acid, and the considerable length of time during which it remains in the acid mixture, and until removed from the endless chain, the desired change of the cotton into nitrated product is produced; by the continuous working of the apparatus, the patentee alleges, a considerable saving in time and labor and a large increase in the productive capacity of the apparatus is obtained.

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[1] E. P 4769, 1895; abst. J. S. C. I. 1895, **14**, 332; 1896, **15**, 68, 134; Chem. Centr. 1896, **67**, I, 1150; Chem. Ztg. 1896, **20**, 652; Chem. Tech. Rep. 1896, **35**, 498. Belg. P. 237894, 1911. In the method of A. Hart (E. P. 18606, 1911; abst. J. Soc. Dyers and Color. 1912, **28**, 38) the cellulose in the form of clean fiber is first stirred for four hours in a 1% sulfuric acid bath. The nitrating bath is prepared of one part of sulfuric acid, sp. gr. 1 84, nitric acid, sp. gr. 1.55 and 20% water, then after standing for fourteen hours the fiber is stirred into this bath in the proportion of one pound of cellulose to one gallon of acid. It is then washed with water until neutral, hydro-extracted and dried by hot air at 82°. The author's experience is that on account of friction and electricity it would be decidedly dangerous to dry nitrocellulose by hot air at the temperature above stated.

[2] U. S. P. 483709; abst. J. A. C. S. 1892, **14**, 319. Cf. Sudenburger Maschinenfabrik und Eisengieserei, D. R. P 58381; abst. Zts. ang. Chem. 1891, **4**, 683; Chem. Ztg. 1891, **15**, 1640; 1892, **16**, 1279; Chem. Tech. Rep. 1891, **30**, II, 255; Chem. Ind. 1892, **15**, 40; Wag. Jahr. 1891, **37**, 430; Ber. 1892, **25**, 240; Meyer Jahr. Chem. 1891, **1**, 332; Tech. Chem. Jahr. 1891, **14**, 137. J. Blomen and H. Aspinwall, U. S. P. 674159, 1901; abst. J. A. C. S. 1902, **24**, 106; Mon. Sci. 1901, **57**, 287. U. S. P. 674291, 1901; abst. J. A. C. S. 1902, **24**, 106; Mon. Sci. 1901, **57**, 287.

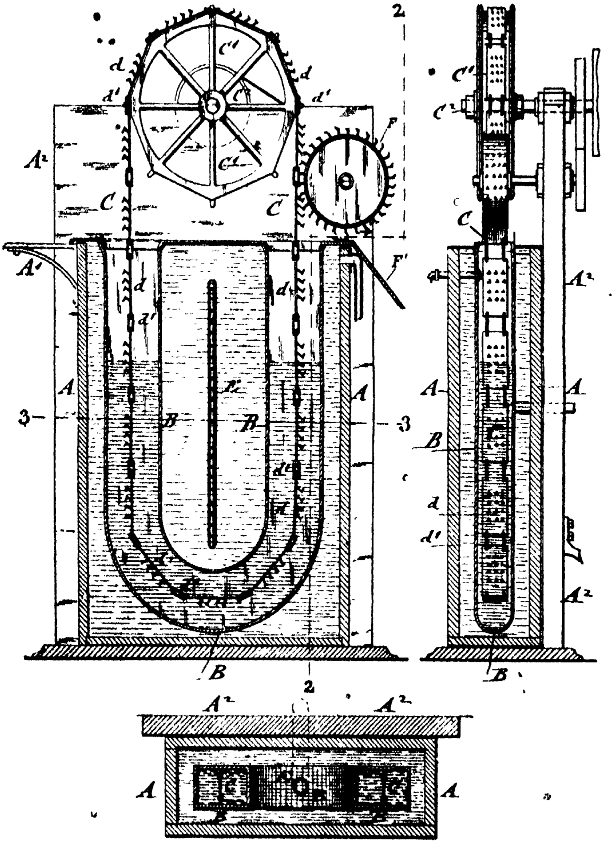

FIG. 190.—BECK AND NENNINGER GUNCOTTON APPARATUS

So far as the author is aware, this method has never been tried commercially, or is unable to locate working datum.

In the process of manufacture of nitrocellulose for war, mining or general purposes as disclosed in the protected application of J. Bantock,[1] clean cellulose is first steeped in a mixture of nitric and sulfuric acids and sodium or potassium sulfate. The liquor is afterwards drained off and the product washed with water. Potassium nitrate or chlorate or other oxidizing salts are added to the cellulose, after which the neutral guncotton is saturated under pressure, the whole being maintained at a temperature sufficient to retain all of the oxidizing salts in solution. The mass is digested for a few hours, after which the excess of solution is filtered off by the aid of a vacuum pump and the mass of nitrocellulose left on the filter until dry. The object of adding nitrates and chlorates is stated by the patentee to increase the disruptive force of the guncotton. (See the topic "Nitrated and Chlorated Guncotton.")

E. Berl[2] has described a process for obtaining nitrocellulose, and claimed to be particularly suitable for the manufacture of artificial silk and powder for explosives. The cellulose, previous to nitrating, is subjected for a considerable time to a high temperature in the presence of inert gases free from oxygen, such as oven gases, water gas, carbon dioxide, nitrogen or superheated steam. If cotton is heated for four days to 120°, at the same time avoiding oxidation, a nitrocellulose is obtained from it on nitration with a mixture of sulfuric and nitric acid and containing $11^1/_2\%$ of water, said nitrocellulose containing as high as 13.5% nitrogen. If the cotton is dried for six hours at 100° and is then nitrated in the manner above stated, a product of the same nitrogen content is said to be obtained. However, when both products are dissolved in known solvents, or solvent mixtures of the same concentrations, solutions will be obtained the viscosity of which

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[1] E. P. 4806, 1876. For nitration of cellulose by electricity, consult G. de Brialles, Can. P. 106374, 1907. Australia P. 5566, 1906. Aust. P. 35080, 1908. F. P. 364349, 1906; abst. C. A. 1907, **1**, 2326; Mon. Sci. 1907, **67**, 93. Swiss P. 36176, 1906. E. P. 2902, 1906; abst. C. A. 1907, **1**, 907, 925; J. S. C. I. 1907, **26**, 114. D. R. P. 203377, 1906; abst. Chem. Zentr. 1908, **79**, II, 1843; C. A. 1909, **3**, 718; Mon. Sci. 1912, **77**, 96; Chem. Ztg. Rep. 1908, **32**, 657; Jahr. Chem. 1905–8, II, 974; Wag. Jahr. 1908, **54**, I, 430; Zts. ang. Chem. 1908, **21**, 2376; Zts. Schiess. Spreng. 1908, **3**, 434.

[2] D. R. P. 199885, 1907; abst. Mon. Sci. 1911, **74**, 93; J. S. C. I. 1908, **26**, 937; Zts. ang. Chem. 1908, **21**, 2233; Chem. Zentr. 1908, **79**, II, 466; Chem. Ztg. Rep. 1908, **32**, 382; Chem. Ind. 1908, **31**, 454; Wag. Jahr. 1908, **54**, II, 355.

are as 5 to 4. Therefore, by varying the temperature on the one hand and the duration of heating on the other, the viscosity of the solutions may be changed at will within comparatively wide limits. At the same time the raw material, it is claimed, does not undergo any radical or undesirable changes. Artificial filaments obtained from these nitrated products are claimed to be of especial value on account of the homogeneity of the solutions, admitting of forcing the same through microscopic apertures under low pressure.[1]

In the apparatus developed for nitrating cotton as designed by T. Henchman,[2] and shown in Fig. 191, the material is fed to the nitrating tank by a traveling band, *X*, and passes down a chute, *C*, into a space between the grooved rotating cylinder, *d*, and the travelling band, *c*, the latter being formed of a number of slats linked together at their ends. The nitrating material is removed from the cylinder, *d*, by a roller, *l*, and from the band, *c*, by a roller, *k*, and is conveyed by further rollers, *m* and *n*, to squeezing rollers, *o* and *p*, from which it is conducted by a chute, to washing tanks. The cylinder *d*, the bands, and the rollers are rotated from a shaft, *H*. The nitrating tank is traversed by pipes *I*, which communicate with an outer tank containing water for heating or cooling purposes.

In the C. Claessen process of nitration,[3] 100 gm. of cotton and three kilos of nitro sulfuric acid are heated together at 40° to 50°. The mixture, containing a limit of 18% to 20% of water—preferably 19%—and 42% sulfuric acid (35% to 46%), 39% nitric acid (35% to 45%), is nitrated during a period of two hours, the temperature not being allowed to rise over 50°. After nitration, wringing, washing in cold water, followed by washing in weak alkaline solution and then to neutrality, there is formed a white amorphous nitrated product containing 9.5% to 10.5% nitrogen and which is readily soluble in 96% alcohol. It gives, when subjected to the action of polarized light, no evidence of un-nitrated fibers. This product is claimed to be especially useful for the manufacture of celluloid when combined with those

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[1] Ber. 1906, **39**, 3901; abst. J. S. C. I. 1906, **25**, 1213; C. A. 1907, **1**, 424; Chem. News, 1907, **95**, 36; J. C. S. 1907, **92**, i, 27; Bull. Soc. Chim. 1907, **2**, 482; Rep. Chim. 1907, **7**, 151; Chem. Zentr. 1907, **78**, I, 153; Chem. Ztg. Rep. 1907, **31**, 46; Chem. Zts. 1907, **6**, 305; Jahr. Chem. 1905-8, II, 1593; Meyer Jahr. Chem. 1906, **16**, 172.

[2] E. P. 2645, 1899; abst. J. S. C. I. 1900, **19**, 71. D. R. P. 114415; abst. Wag. Jahr. 1900, **46**, I, 395.

[3] D. R. P. 163668, 1904; abst. Mon. Sci. 1906, **65**, 159; Chem. Centr. 1905, **76**, II, 1568; Chem. Ztg. 1905, **29**, 942; Jahr. Chem. 1905-8, II, 992; Wag. Jahr. 1905, **51**, II, 570; Zts. ang. Chem. 1906, **19**, 204.

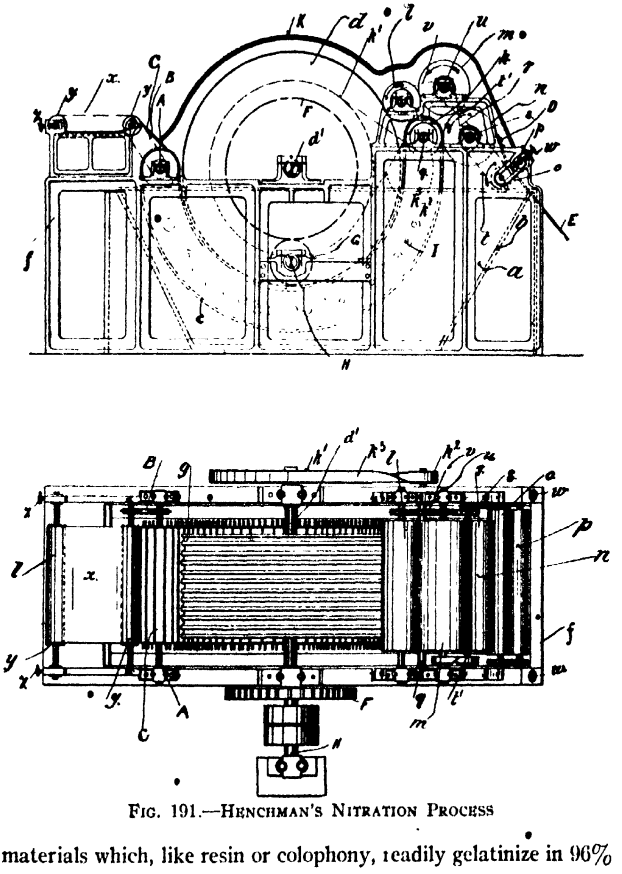

FIG. 191.—HENCHMAN'S NITRATION PROCESS

materials which, like resin or colophony, readily gelatinize in 96% alcohol.

P. Prost and E. Micehy[1] form a non-inflammable nitrated product containing a low percentage of nitrogen by treating cellulose with a mixture of three parts of sulfuric acid to one part of nitric acid until superficially nitrated only, the product being afterwards dissolved in alcohol and ether, or acetone, to which from 1%–20% of zinc, iron, aluminium or ammonium chlorides or alum have been added. The solvent is then distilled off and the plates of material pressed and treated in a bath of sodium carbonate or sodium silicate to further reduce the inflammability.

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[1] E. P. 5130, 1905.

In the process as recommended by the Zellstoff-fabrik Waldhof,[1] dry cellulose is freed from incrusting matter and other soluble constituents in the usual way, and is then reduced to such a degree of fineness by means of a carding machine, or preferably by means of an arrangement as shown in Fig. 192, that, by treatment of the material with nitro-sulfuric acid, a nitrate is obtained which, it is claimed, is not decomposed at a temperature of 70°. In a section through the reducing machine illustrated, the plates *dd*, are carried by the hubs *a* and *b*, which are rotated at a high speed, the material passing down the hopper *e*, and being carried by centrifugal action between the bin *c* and the plates *dd*.

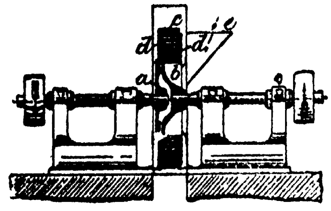

FIG. 192.—COTTON NITRATION PROCESS ZELLSTOFF-FABRIK

To obtain a nitrocellulose paste especially applicable for smokeless powder use, and of a constant composition of 12.7% nitrogen, P. Joliot[2] employs "regenerated cellulose," that is, cellulose obtained from the reduction of cuproammoniacal cellulose, or that obtained by reduction from cellulose xanthate (viscose). The product obtained is claimed to be completely soluble in ether-alcohol and to yield a smokeless powder of more constant character than when made from ordinary cellulose. No datum as regards stability is given by the patentee.

In 1907 there was granted protection to J. Schneider in England,[3] for a process for production of cellulose esters in which cotton or other vegetable material is treated with a mixture of sulfuric and nitric or acetic acids carrying varying amounts of water; those with mixed nitric and sulfuric acids containing less than about 25% of water. Nitrocelluloses are said to be obtained which are soluble in alkali, insoluble in sulfuric acid, resist direct dyes, but have an affinity for basic dyes. Considerable dilution of the acids gives rise to a form of cellulose to which the name "Cellulose-S" is given, and which is insoluble in alkali but soluble in sulfuric acid, resists the action of basic dyestuffs, but has a direct affinity for substantive cotton colors. The acid mixtures are made in iron or stoneware vessels, and the material, preferably unbleached and dry, is steeped in this mixture, keeping the temperature at 70° for several hours. As the acid mixture is taken up by the cellulose it is replaced by a fresh solution. After this process of steeping, the product is squeezed, hydroextracted and washed with dilute sodium carbonate until all acid is removed. Stability tests made with potassium iodide starch solution or zinc iodide starch paper are stated to have been very satisfactory.

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[1] E. P. 336, 1891; abst. J. S. C. I. 1891, **10**, 86, 1052; 1892, **11**, 180; Mon. Sci. 1892, **40**, 166.

[2] F. P. 468337, 1913; abst. Mon. Sci. 1916, **83**, 68.

[3] E. P. 3645, 1907; abst. J. S. C. I. 1908, **27**, 332; C. A. 1908, **2**, 2626; Chem. Ztg. Rep. 1908, **32**, 180.

G. Klie has found the following method insures a uniformly soluble cotton being produced, especially suitable for surgical and pharmaceutical uses.[1] There are mixed 7.25 ounces of granular potassium nitrate in a mortar, with 6.75 fluid ounces of sulfuric acid, to which are added 180 grains of cotton, free from impurities. After standing twelve to fifteen hours, washing the product thoroughly, first with cold water and then with boiling and drying, a nitrated product is said to result of unusually thin flowing properties, readily soluble in alcohol and ether and to be especially applicable for sealing wounds and abraded surfaces.

Mainly of historical interest is the process of J. Revy[2] patented in 1865, which had for its object improvements in the manufacture of explosive compounds, especially nitrocotton. In the process as described by him, ordinary cotton is spun, by the aid of machinery, into a lightly twisted yarn which is rendered absorbent and then nitrated by means of a mixture of nitric acid of specific gravity 1.52 and sulfuric acid of specific gravity 1.84. The acids are poured upon the cotton separately, at the same time mechanical agitation being provided. After nitration, the product is washed free from acid in the usual manner, boiled in a solution of potassium silicate (water glass), washed with water, and finally dried at a low temperature.

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[1] Proc. Amer. Pharm. Assoc. 1877, **25**, 286; abst. Amer. J. Pharm. 1877, 301.

[2] U. S. P. 50082, 50083, 1865. E. P. 2720, 1863. See E. P. 1090, 1862. Cf. A. Luck and C. Cross, Belg. P. 138487, 1898. Soc. anon. des plaques et Papiers photographiques, A. Lumiére et fils., F. P. 361324; abst. C. A. 1907, **1**, 962, 1082; Mon. Sci. 1906, **65**, 169; 1907, **66**, 599.

In the H. de Chardonnet method,[1] developed primarily for the manufacture of artificial silk and other filaments, the nitration is effected in the ordinary manner, the nitrocellulose and mixture of acids being placed in a centrifugal machine, by which means about three-quarters of the acid is recovered after nitration and may be used again after strengthening. The acids remaining in the nitrocellulose are then removed by washing, the washings neutralized with lime and the solution of calcium nitrate decomposed by sodium sulfate. The sodium nitrate thus obtained is utilized again for the production of nitric acid. The nitrocellulose is further bleached with a dilute solution of bleaching powder, the inflammability being reduced by a final process of de-nitration, effected by means of warm nitric acid, alkaline sulfides or sulfo-carbonates. The apparatus is shown in Fig. 193.

The process of J. Arrault and J. and C. Schmerber[2] was developed for the purpose of decreasing the amount of nitric acid required in the nitration process. In the preferred method as described by them, nitro derivatives of cellulose, starch and glucose are obtained by the employment of nitric acid especially in a gaseous state by which process practically little more acid than the theoretical quantity required to transform the substances into their esters is said to be required. There is claimed, therefore, for this process great economy. In carry-

[1] E. P. 5376, 1890; abst. J. S. C. I. 1891, **10,** 566 E. P. 19560, 1891; E. P. 24638, 1893; abst. J. S. C. I. 1891, **10,** 971; 1892, **11,** 798, 939; 1894, **13,** 86, 1123; 1895, **14,** 33. F. P. 201740, 1889; 216564, 1891; abst. Mon. Sci. 1890, **35,** 550, 1212; 1891, **38,** 1243; 1892, **39,** 289; 1905, **62,** 321; Rev. Chim. Ind. 1890, **1,** 76; Tech. Chem. Jahr. 1889, **12,** 161. D. R. P. 64031, 1891; abst. Zts. ang. Chem. 1892, **5,** 499; Chem. Centr. 1892, **63,** II, 1088; Chem. Ztg. 1892, **16,** 1432; 1893, **17,** 1004; Chem. Tech. Rep. 1892, **31,** II, 164; Chem. Ind. 1892, **15,** 485; Wag. Jahr. 1892, **38,** 376; Ber. 1892, **25,** 892-R; Mon. Sci. 1892, **40,** 166; Industriebl. 1892, 358; Meyer Jahr. Chem. 1892, **2,** 362; Tech. Chem. Jahr. 1892–3, **15,** 169.

[2] U. S. P. 230216, 1880; abst. J. A. C. S. 1880, **2,** 354. In this connection see A. Colassi, F. P. 490935, 1919; abst. Chim. et Ind.

ing out the method, the apparatus used may consist of an air-tight chamber in which the cellulose to be nitrated is exposed to the gaseous nitric acid, the latter being produced in a separate apparatus, as by treatment of a nitrate with sulfuric acid. By regulation of the quantity of nitric acid and the temperature, nitro derivatives of different physical characteristics result, as the gaseous acid is claimed to penetrate and mix intimately with every particle of the substance subjected to its action, so that the conversion takes place with the use of but slightly more than the theoretical quantity required to transform cellulose into the dry nitro derivative. No process at the present day, so far as aware, is being used with nitric acid gas produced in this manner.

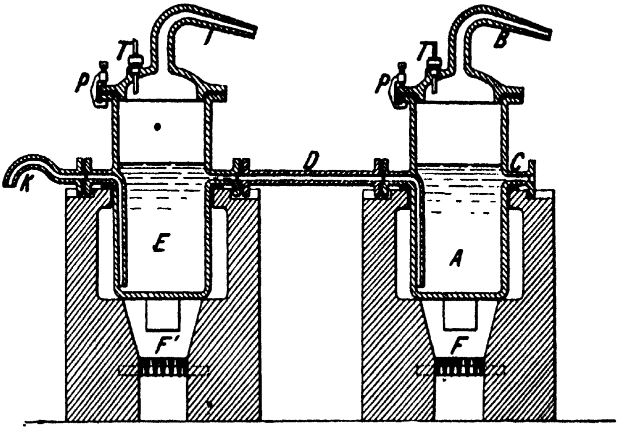

FIG. 193.—CHARDONNET NITRATING APPARATUS

Carl Ditmar[1], in endeavoring to produce a granular nitrocellulose for explosive purposes without the use of colloiding agents upon the nitrated material, first reduced cellulose to a pulp similar to the pulp used for the manufacture of paper, and after removing any extraneous matter, the material was dipped in a bath of sulfuric acid in the proportion of ten pounds of acid of commerce to one pound of water, and immediately, or within a minute or two afterwards, subjected it to a washing process with water to remove the acid. In this way the pulp became partially or completely parchmentized and upon drying and subjecting to a bath of nitric and sulfuric acids, the cotton, in a more or less granular form, became converted, according to the statement of the patentee, into the desired form of guncotton.

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[1] U. S. P. 179688, 1875. E. P. 3088, 1875; abst. Ber. 1877, **10**, 725; Wag. Jahr. 1877, **23**, 284. F. P. 109449; abst. Bull. Soc. Chim. 1876, **26**, 525; Mon. Sci. 1876, **18**, 1094. C. Hofmann and H. Josephy (D. R. P. 292543; abst. Chem. Zentr. 1916, **87**, II, 113; Chem. Ztg. Rep. 1916, **40**, 237; Wag. Jahr. 1916, **62**, II, 12; Zts. ang. Chem. 1916, **29**, 323) replaced the sulfuric acid in the nitrating bath by ortho-, meta-, or pyro-phosphoric acids.

C. Cross, E. Bevan and C. Beadle have patented a method for nitrating cellulose which consists in first producing products such as hydrocellulose or oxycellulose by subjecting air-dried, bleached fibers to the action of hydrochloric acid gas for some hours in a closed chamber, then washing the fibers with water until free from acid, and finally drying and dissolving them in concentrated nitric acid to form a clear, gummy solution. Nitrates of various degrees of nitration may be prepared from this solution, according to the patentees, by precipitating with water for the lower nitrates, or with sulfuric acid for the higher nitrocelluloses.[1]

In the nitration of cellulose and its derivatives as pointed out by the Deutsche Celluloid fabrik,[2] the former practice of operating with nitric acid generated from potassium nitrate or sodium nitrate and sulfuric acid and under the normal pressure, has proven impracticable, because at the normal pressure too high temperatures were required, resulting in the decomposition of the cellulose, while the nitration did not proceed uniformly. These difficulties, it is claimed, may be obviated by operating in a high vacuum at temperatures not exceeding 50°. A uniformly nitrated product is stated to result in quantitative yield regardless of the surrounding temperature and moisture. Products of any desired nitrogen content may also be obtained. The material can be dried, nitrated and washed in the same apparatus without mechanically mixing and stirring appliances or complicated devices, while, at the same time, the operator is protected from injurious fumes, and the dilute nitric acid resulting from the process can be removed without difficulty, and subsequently be reclaimed.

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[1] E. P. 9284, 1892; abst. J. S. C. I. 1892, **11**, 566, 668; 1893, **12**, 92, 400; Chem. Centr. 1893, **64**, II, 702. T. Hawkins, Australia P. 19452, 1910, The Hermite and Dubosc process of cellulose nitration, is detailed in Bull. Soc. Ind. Rouen, 1902, **30**, 244.

[2] D. R. P. 269246, 1912; abst. C. A. 1914, **8**, 2060; J. S. C. I. 1914, **33**, 335; Chem. Zentr. 1914, **85**, I, 595; Chem. Ztg. Rep. 1914, **38**, 66; Wag. Jahr. 1914, **60**, I, 359; Zts. ang. Chem. 1914, **27**, 167. D. R. P. Anm. 26485; abst. Chem. Ztg. 1913, **37**, 430. R. Adler, D. R. P. 283304, 1913; abst. C. A. 1915, **9**, 3360; Chem. Zentr. 1915, **86**, I, 864; Chem. Ztg. Rep. 1915, **39**, 220; Wag. Jahr. 1915, **61**, II, 14; Zts. ang. Chem. 1915, **28**, 244. A. Klein, Zts. ang. Chem. 1907, **20**, 610; Chem. Centr. 1907, I, 1557; C. A. 1907, **1**, 485, 2492. For the nitration apparatus of Wülfing, Dahl & Co., and H. Wyler, see D. R. P. 300079, 1915; abst. Chem. Ztg. 1920, **44**, 393.

The F. Greening process[1] especially designed for the preparation of pyroxylin compounds useful for waterproofing textile fabrics, consists, first, in the employment of hydrochloric acid to convert the cotton or other ligneous fibers, in addition to or in conjunction with the sulfuric and nitric acids generally employed. In carrying out this invention, the cotton is submitted to a mixture of acids, as before mentioned, the conversion taking place preferably at a temperature not exceeding 25°. After the conversion has been effected the product is washed with water, until the last traces of acid are removed, then submitted to a dilute alkaline bath, and finally washed. The products so obtained, when dissolved in volatile solvents, are claimed to be especially applicable for the formation of artificial leather when spread upon textiles.

The M. Kaltenbach process for the nitration of cellulose,

[1] U. S. P. 172995, 401269. E. P. 2481, 1883; abst. Wag. Jahr. 1884, **30**, 1204. E. P. 8442, 1886; abst. J. S. C. I. 1886, **5**, 441; 1887, **6**, 549. E. P. 2044, 1875. E. P. 5344, 1889; abst. J. S. C I. 1889, **8**, 320; 1890, **9**, 236, 522. E. P. 22019, 1894; abst. J. S. C. I. 1896, **15**, 124; Chem. Centr. 1896, **67**, I, 1150. F. P. 110571; abst. Mon. Sci. 1876, **18**, 1095. F. P. 184247; abst. Mon. Sci. 1888, **31**, 632. Belg. P. 77879. The L. Guiguet process (F. P. 464028, abst. C. A. 1914, **8**, 3122; Mon. Sci. 1916, **83**, 67; Chem. Ztg. 1914, **38**, 363) is for the nitration of linters. For hydrolysis of cellulose previous to nitration see H. Arledter, E. P. 16085, 1912; abst. C. A. 1914, **8**, 247; J. S. C. I. 1913, **32**, 865.

In the process of Gillet & Co. (E. P. 136568, 1920) cotton is given a luster approaching that of real silk by superficial or partial nitration by impregnating the fibers with nitric acid of above 65% in strength at temperatures above 12° and under 25°, and in precipitating upon the fibers a slightly nitrated cellulose by washing the treated fibers with water. The product which is deposited upon the fiber is said to contain about 5–6% N. In examples given by the patentees to show the preferred manipulation of their process, 30 gm. wood pulp or cotton waste are introduced rapidly and with constant stirring into 1000 gm. 83% HNO_3 at a temperature of 15–20°, and after complete solution to a syrupy mass, 112 gm. water are added. The product is intended primarily to be deposited on cotton fabrics to enhance the luster. The reaction is said to take place as easily at 0° as at 25°, but as the solutions become more and more viscous with the fall of temperature, it is advantageous in practice to work at temperatures between 12° and 25°.

as patented in France,[1] is shown in Fig. 194. In manufacturing nitrocellulose by the J. Boursin method,[2] a constant low temperature is maintained in the jackets of an apparatus, which is attained by filling it with an alloy which has a low melting point and providing the alloy in sufficient quantity and with enough radiating surface to carry off the surplus heat without all of the alloy being melted.

In the process of E. Quinan,[3] cellulose fiber is first dipped in a bath of hot nitric acid in order to dissolve the mineral substances contained therein, the product being next washed in a weak acid solution in order to remove the dissolved matter and then heated to complete the transformation of cellulose into hydrocellulose whereupon it is powdered and subsequently nitrated.

R. Schonlau[4] nitrates with four parts of 40° Bé. nitric acid to 9.3 parts 66° Bé. sulfuric acid, by weight, after which the nitrated cotton is plunged into a mixture of four parts of 61% nitric acid and 9.3 parts sulfuric acid of 93.5% strength, in which the nitration is allowed to proceed for several hours in order to produce a more stable ester. Nitrocellulose obtained by this process is said to be readily soluble in acetone, ethyl acetate and in a mixture of alcohol and ether and to have special advantages for the production of celluloid and similar thermoplastic nitrocellulose combinations.

E. Müller[5] has been granted a patent in England which relates to an apparatus for nitrifying cellulose (Fig. 195)

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[1] F. P. 453588, 1913; abst. C. A. 1914, **8**, 251; Kunst. 1913, **3**, 416; J. S. C. I. 1913, **32**, 768; Chem. Ztg. Rep. 1913, **37**, 572.

[2] E. P. 24696, 1908. See Vereinigte Kunstseidefabriken A. G., Ital. P. 132230, 1913. See Soc. Gen. pour la Fabr. des Matiere Plastiques, E. P. Appl. 20283, 1917. F. P. Dec. 6, 1917.

[3] D. R. P. 117349, 1898; abst. Mon. Sci. 1901, **57**, 148; Chem. Centr. 1901, **72**, I, 288; Chem. Ztg. 1901, **25**, 93; Jahr. Chem. 1901, **54**, 895; Wag. Jahr. 1901, **47**, I, 492; Zts. ang. Chem. 1901, **14**, 117. See Zellstoff-fabrik Waldhof, D. R. P. 64878, 1890; abst. Mon. Sci. 1893, **41**, 208; Ber. 1893, **26**, 78-R; Wag. Jahr. 1892, **38**, 371; Zts. ang. Chem. 1892, **5**, 706. Processes similar to that of G. Wolf (Russ. Zts. Pharm. **22**, 4; Jahr. Chem., 1883, **36**, 1779), in which nitrates, as KNO_3, are employed with sulfuric acid have long since been abandoned, due to the prolonged washing required to eliminate the alkaline sulfate formed by double decomposition. C. Quinan, U. S. P. 597565, 1898; abst. Mon. Sci. 1898, **52**, 178; Chem. Ztg. 1898, **22**, 106. I. Moscicki, Belg. P. 194363, 1906.

[4] F. P. 469484, 1914; abst. J. S. C. I. 1915, **34**, 24. Swiss P. 60990, 1912.

[5] E. P. 8843, 1890; abst. J. S. C. I. 1890, **9**, 686, 998, 1064.

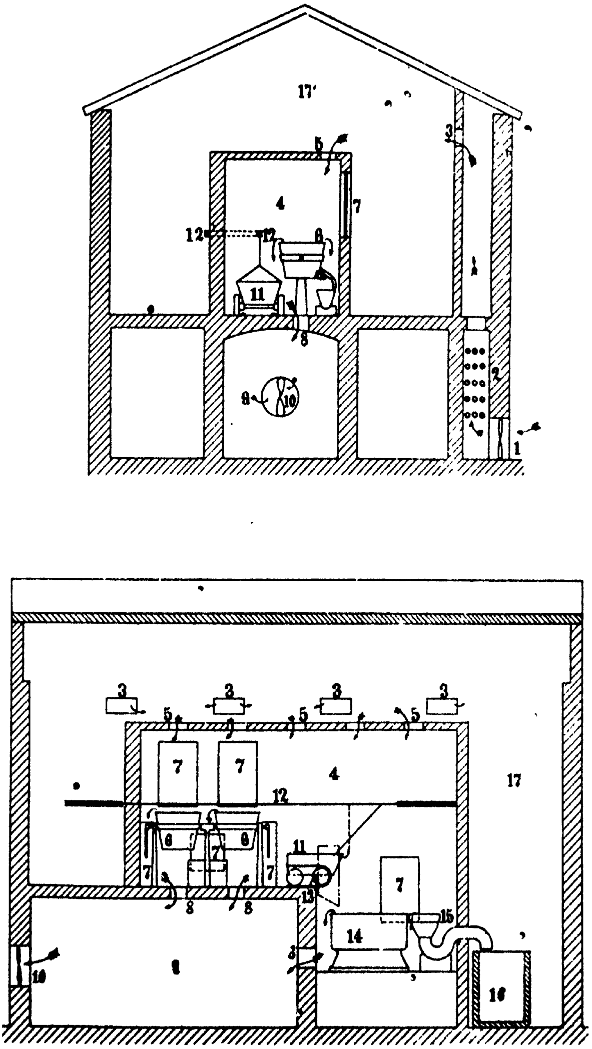

FIG. 194.—KALTENBACH NITRATION PROCESS

in which the acid is admitted to the vessel *A*, containing the cellulose, through the pipe *R*, from the acid vessel *C*. When esterification has been completed the acid is returned to the vessel *C* by connecting pipe R^1, to an air pump, the acid being withdrawn through the pipe *H*. The apparatus of the Rheinische Westphalische Sprengstoff A-G[1] is similar.

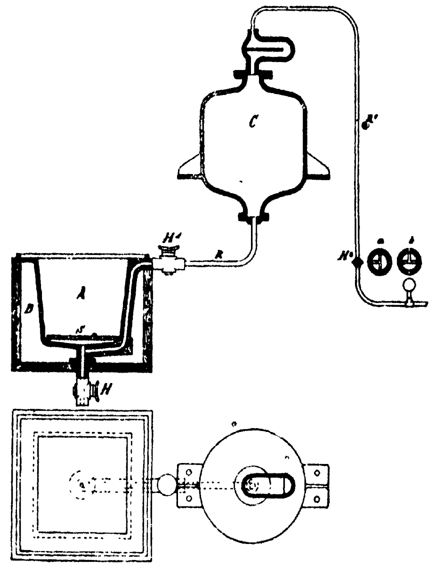

FIG. 195.—MÜLLER PROCESS FOR COTTON NITRATION

T. Henchmann[2] provides a chain upon which the material to be nitrated is pressed by means of a drum provided with rifling on its circumference, the chain being then conducted through a cylindrical vessel filled with a nitrating acid and surrounded with a jacket for cooling and heating, the chain being finally conducted toward brush-like rotating cylinders which strip the material from the chain after nitration.

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[1] D. R. P. 54077; abst. Zts. ang. Chem. 1890, **3**, 713; Chem. Ztg. 1890, **14**, 1638; 1892, **16**, 277; Chem. Tech. Rep. 1890, **29**, II, 144; Wag. Jahr. 1890, **36**, 539; Ber. 1890, **23**, 718-R; Tech. Chem. Jahr. 1890–1, **13**, 153; Meyer Jahr. Chem. 1891, **1**, 332; Dingl. Poly. 1891, **282**, 61. Ital. P. 32338, 1892.

[2] D. R. P. 114415; abst. Wag. Jahr. 1900, **46**, I, 395.

A. Dufay[1] proposes a method in which the cellulose is treated with a mixture of nitrogen pentoxide and nitric acid, and describes the method of preparing both nitrogen pentoxide and nitric acid by the aid of P_2O_5. According to Dufay the substitution of N_2O_5 for the sulfuric acid, usually employed in nitration, prevents the formation of sulfuric esters, while "since the reaction occurs in the nitric medium there is no fear of secondary reactions."

The L. Morane apparatus[2] shown in Fig. 196 offers the advantage that all the operations of nitration up to the moment when the nitrocellulose is plunged into water, are effected

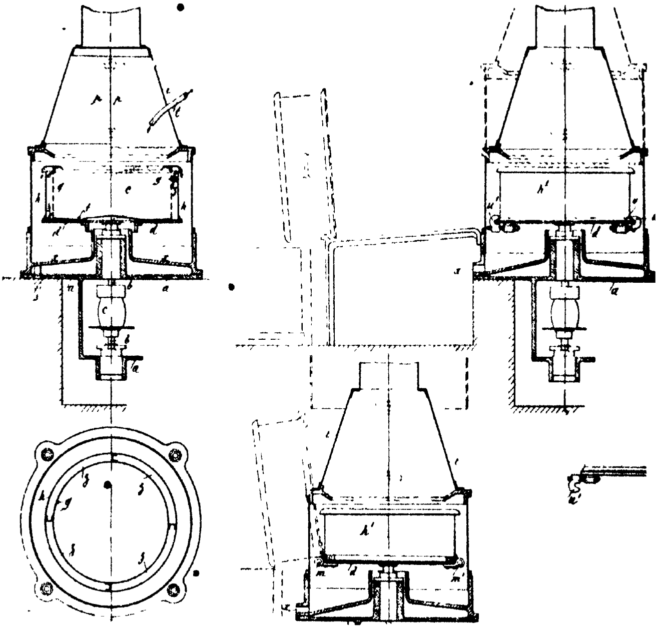

Fig. 196.—The Morane Nitrating Apparatus

in one apparatus which, at the same time, is closed but yet is in communication with a ventilator whereby the acid vapors are driven into a condenser. In this manner, according to the patentee, no acid vapors escape into the atmosphere of the work room or to the exterior. Draining, and the removal to the press or centrifugal apparatus is thereby obviated and the work rendered more rapid and without the nitrated cotton coming into contact with the atmosphere, thus tending to obtain an increased yield.

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[1] Chem. News, 1912, **106**, 211; abst. C. A. 1913, **7**, 1418.

[2] E. P. 24561, 1899; abst. J. S. C. I. 1900, **19**, 375.

L. Bethisy[1] advocates the addition of nitric and sulfuric acids to cellulose in the proportion of 24 kilos nitric acid 42° Bé. to 56 kilos sulfuric acid, 66° Bé., as this mixture brings about a rise in temperature. The vessels are preferably immersed in a current of cold water where they are covered and left to stand until the temperature sinks to 30°. Cellulose is then added to the above mixture of acid in the proportion of 5 to 6 kilos.

L. Labbe[2] employs for 100 gm. of cotton, 950 cc. of nitric acid of sp. gr. 1.457, 2550 cc. sulfuric acid, sp. gr. 1.845, and 750 cc. of water, maintaining the temperature at 60°, the time of immersion being ten minutes.

G. Aschas[3] nitrates cellulose with a cooled mixture of 3 parts sulfuric and one part of highly concentrated nitric acids, while H. Danzer[4] employs equal parts, by weight, of nitric acid of 38° Bé. and sulfuric acid of 66° Bé., immersing the cotton in the nitrating bath when the latter has been cooled to 25° or lower.

The nitration processes of J. Reeves,[5] F. Glaser,[6] A. Martin,[7] and the methods of Kostanezki,[8] Kral,[9] and J. Schulhof[10] offer

[1] E. P. 11397, 1907; abst. C. A. 1909, **3**, 122; J. S. C. I. 1908, **27**, 640. F. P. 347303, 1904; abst. C. A. 1907, **1**, 358; Mon. Sci. 1906, **65**, 112; Chem. Zts. 1905, **4**, 89.

[2] F. P. 410973, 1910; abst. Mon. Sci. 1912, **77**, 7.

[3] Swiss. P. 11964, 1899; abst. Mon. Sci. 1901, **57**, 287.

[4] F. P. Add. 13659 to 410725, 1911.

[5] E. P. 989, 1867. See also F. Reeves and J. Muschamp, E. P. 3293, 1866.

[6] E. P. 17167, 1887; abst. J. S. C. I. 1888, **7**, 867.

[7] Les Mondes, 1873, 30.

[8] Zts. Pharm. Russ. **22**, 65; abst. Jahr. Chem. 1883, **35**, 1779.

[9] Poly. Notiz. 1865, **20**, 304. Chem. Centr. 1865, **36**, 258; Poly. Centr. 1865, **31**, 1519; Wieck's Gewerbeztg. 1865, 355; abst. Wag. Jahr. 1865, **11**, 413.

[10] E. P. 4917, 1882; abst. Les Mondes 1884 (3), **7**, 321; Chem. Ind. 1883, **6**, 375; Ber. 1883, **16**, 2941; Jahr. Chem. 1883, **36**, 1705; Pharm. Rundschau, 1883, 759; Chem. Tech. Rep. 1883, **22**, I, 201; II, 190; Poly. Notiz. 1884, **39**, 76; Wag. Jahr. 1884, **30**, 377. E. P. 1767, 1883; abst. J. S. C. I. 1883, **2**, 191. U. S. P. 304361; abst. J. A. C. S. 1884, **6**, 374.

nothing new, so far as ascertainable from the patents.

According to W. Crombie,[1] a nitrocellulose consisting solely of soluble nitrated cotton and containing a high percentage of nitrogen, may be prepared by making the nitrating bath of 58 parts sulfuric acid, 29 of nitric acid, and 13 parts of water. R. Annison and G. Oliver[2] limit the period of nitration to 10 minutes. In the method of G. Fayt,[3] the cotton is introduced and removed from the nitrating bath continuously by means of an Archimedean screw rotating in a drum-shaped container, surrounded by an envelope for heating or cooling.

A. Hollings[4] links the cotton together and then nitrates in a continuous manner by means of an arrangement patented by him. In the A. Liedbeck process,[5] cellulose is simultaneously nitrated and ground in a beater in order to obtain a more uniform product. A. Müller-Jacobs[6] nitrates cellulose in rolls of cloth, and forms an explosive therefrom by printing on the nitrated fabric with a solution of ammonium picrate and potassium chlorate, together with a suitable adhesive.

The Aktienges. Dynamit Nobel[7] seek to obtain a more uniform result while nitrating, by exhausting the nitrating vessel, a part of the acid constantly being renewed by fresh acid, which tends to keep down the temperature. This is the opposite of the

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1. E. P. 19074, 1898; abst. Arms and Expl. 1899, **7,** 158; Mon. Sci. 1900, **55,** 131; Chem. Ztg. Rep. 1900, **24,** 20.

2. E. P. 4577, 1906; abst. C. A. 1907, **1,** 1773, 1788, J. S. C. I. 1907, **26,** 340; Zts. Schiess. Spreng. 1907, **2,** 195.

3. Belg. P. 241341, 1911.

4. E. P. 13278, 1899; D. R. P. 122608; abst. Arms and Expl. 1900, **8,** 131; Chem. Ztg. Rep. 1901, **25,** 875; Wag. Jahr. 1901, **47,** I, 494, Zts ang. Chem. 1901, **14,** 956; J. S. C. I. 1900, **19,** 775.

5. E. P. 14690, 1897; Belg. P. 128925, 1897; U S. P. 718484, 1903, D. R. P. 96109, 111289; E. P. 27397, 1898; F. P. 285488, 1899, Swed. P. 8049, 1896; abst. J. S. C I. 1897, **16,** 760; 1899, **18,** 401; 1903, **22,** 165; Mon. Sci. 1898, **52,** 94; 1899, **54,** 189; 1901, **57,** 29; Chem. Centr. 1898, **69,** I, 1222; 1900, **71,** II, 231; Chem. Tech. Rep. 1898, **37,** 221; Chem. Ztg. 1900, **24,** 504; Jahr. Chem. 1898, **51,** 1382; Zts. ang. Chem. 1900, **13,** 525

6. E. P. 27162, 1904; abst. Arms and Expl. 1905, **13,** 37; J. S. C. I. 1905, **24,** 250.

7. D. R. P. 4410, 1878; abst. Dingl. Poly. 1879, **232,** 188; Zts. Chem. Grossgewerbe, 1879, **4,** 287; Deut. Industrieztg. 1879, 170; Ber. 1879, **12,** 712; Chem. Ztg. 1879, **3,** 197; Wag. Jahr. 1879, **25,** 419; Chem. Ind. 1879, **2,** 171; Chem. Tech. Rep. 1879, **18,** I, 287; J. A. C. S. 1879, **1,** 303; Chem. Tech. Mitth. 1878–9, **28,** 295. D. R. P. 74736; abst. Zts. ang. Chem. 1894, **7,** 340; Chem. Ztg. 1894, **18,** 1090; Chem. Tech. Rep. 1894, **33,** I, 239; Wag. Jahr. 1894, **40,** 496; Ber. 1894, **27,** 777-R; Meyer Jahr. Chem. 1894, **4,** 418; Tech. Chem. Jahr. 1894–5, **17,** 172; Jahr. Chem. 1893, **46,** 1133.

older A. Parkes process,[1] *where the nitrating acids were removed by pressure. In the manufacture of an explosive combination, S. Mackie, C. Faure and G. Trench*[2] *first nitrate in the usual manner, then neutralize the waste nitrating acid with barium carbonate, filter off the barium sulfate, and incorporate the* barium nitrate with the nitrated cellulose as a finished explosive. T. Shaffner both nitrates and washes under pressure in order to cause more intimate contact with the acids, and to facilitate their removal after esterification.[3] A. Voswinkel[4] first treats with zinc chloride to facilitate esterification, then with fuming nitric acid at a temperature of 10°–15°. A. Vogel[5] reduces the period of nitration to five minutes.

In the apparatus of Wunderlich,[6] stirrer arms are so arranged that the material to be nitrated is seized by them and propelled along the base of a corrugated false bottom, at the end of which it is seized by a perforated drum and a roller, which pulls it out of the nitrating bath. The acid is squeezed out and is returned through the perforated bottom into the apparatus.

Nitration of Cotton for Cheaper Grades of Pyroxylin. In nitrocellulose intended for combination with oils and pigments, in opaque products, especially in bronzing liquids, artificial leather mixtures and pyroxylin coating compositions, where clearness, solubility, viscosity and freedom from insoluble particles are of minor consideration, a grade of cellulose nitrate is made by means of centrifugals which is used in enormous quantities at the present time in the United States. The following is the process in its essentials: The acid mixture used consists of 55% sulfuric acid, 17% nitric acid, water 28%, giving a total acidity of 72%. The initial temperature of the nitrating acid as it comes in contact with the cotton is 46° to 48° but is required to be heated two or three degrees higher to allow for cooling during transmission of the acid to the nitrating centrifuge Fifteen minutes is the time of nitration and five wringers are usually nitrated each two hour period. The heat of reaction raises the contents of the centrifugal to 54°-57°, yield 128% to 135% on the weight of the dry cotton; nitrogen content 12.35%-12.40%; nitrating mixture 35 to 50 times the weight of the cotton immersed. The product is nearly soluble in commercial wood alcohol, contains considerable residue, the majority of which is soluble in acetone, has a low viscosity and thin flow and dissolves readily. The stability is not high. As the temperature of nitration increases the cost rises correspondingly, for the higher nitrating acid means a more fluid pyroxylin, greater loss in washing and neutralizing, more frequent replacement of rubber gloves, etc., and a greater frequency of the batches fuming off in the wringer. The value of this grade of pyroxylin lies in the small amount of solvent necessary to make a workable solution and this is of special value in the imitation leather industry and in the formation of colored films where the solvent is usually not recovered. Raising the sulfuric acid in the nitrating mixture lowers the nitrogen content of the pyroxylin; increasing the percentage of nitric acid, increases the amount of nitrogen in the nitrocotton; elevation of temperature without changing the composition of the nitrating mixture has but little effect on the nitrogen content, although the yield is somewhat diminished and a nitrocotton of greater fluidity is formed.

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[1] E. P. 3163, 1865; abst. Mon. Sci. 1913, **78**, 392.

[2] E. P. 2062, 3612, 1874; abst. Chem. News, 1874, **29**, 166; Ber. 1876, **9**, 205; Bayer. Ind. Gewerbebl. 1876, 141; Zts. Chem. Grossgewerbe, 1876, **1**, 233; Dingl. Poly. 1874, **213**, 174; Poly. Centr. 1874, **40**, 789; Wag. Jahr. 1876, **22**, 480. S. Mackie, U. S. P. 141654, abst. Amer. Chemist, 1873, **4**, 238; E. P. 2693, 1872; abst. Ber. 1874, **7**, 741; Poly. Centr. 1874, **40**, 789; Bayer Ind. Gewerbebl. 1874, 276; Dingl. Poly. 1874, **213**, 174; Chem. Tech. Mitth. 1874–5, 218. F. P. 99589, 1873. Electr. Engineer, 1881, **9**, 260; J. Soc. Arts, 1873, **21**, 470; **23**, 227.

[3] U. S. P. 60571, 1866; 93757, 1869.

[4] D. R. P. 74070; abst. Jahr. Chem. 1894, **47**, 1134; Zts. ang. Chem. 1894, **7**, 307; Chem. Centr. 1894, **65**, I, 1168; Chem. Ztg. 1894, **18**, 612, 1090; Chem. Tech. Rep. 1894, **33**, I, 239; Chem. Ind. 1894, **17**, 512; Wag. Jahr. 1894, **40**, 495; Ber. 1894, **27**, 537-R; Tech. Chem. Jahr. 1893–4, **16**, 165; Meyer Jahr. Chem. 1894, **4**, 418.

[5] Poly. Notiz. 1872, **27**, No. 4; N. Repert. f. Pharm. 1872, 7; Dingl. Poly. 1872, **203**, 504; Pharm. Centralhalle, 1872, **14**, No. 17; Chem. Tech. Mitth. 1871–2, **1**, 48; Jahr. Chem. 1872, **25**, 1083.

[6] D. R. P. 65399, 1891; abst. Mon. Sci. 1893, **37**, 861; Ber. 1893, **26**, 124; Wag. Jahr. 1893, **39**, 427.

Pyroxylin of an inferior grade, as regards color only, can be produced from cotton waste of the trade which is not bleached but simply scoured. Paper made from the sulfite and sulfate processes is capable of yielding a very soluble pyroxylin, which may be nitrated at high temperatures and still yield a notable increase in weight.

Nitration of Paper. The nitrating apparatus of R. Schüpphaus and M. White, G. Mowbray, Tribouillet and de Besauncele and Hyatt, were all designed for the nitration of tissue paper. It has repeatedly been asserted that the finest quality of lacquer and bronzing liquids, transparent plastics and pyroxylin for the preparation of cinematographic and other continuous films, can be obtained only by the nitration of tissue paper. It is a fact that the lightest colored lacquers, the so-called "water-white" grade, are to-day produced in the United States from nitrated tissue paper (so-called paproxyl) in preference to the higher grades of cotton. The actual advantages observed are ease in nitration and speed of penetration, the paper being seldom thicker than 0.003 inch; facility of solution of the nitrated paper; entire absence of cloudiness of the filtered solutions; and the near approach (tintometrically) to forming colorless solutions. It has been pointed out in several works and scientific articles that the high cost of tissue paper must of necessity preclude its use in any large quantities for this purpose, but all, so far as the author is aware, of the manufacturers of pyroxylin plastics in the United States either manufacture or use large quantities of nitrated tissue paper. When the relative cost of a high grade of cotton is calculated as compared with tissue paper at the present day, it is evident that the difference in cost of raw material is not so marked. The ease and completeness with which solid particles may be removed from nitrated paper solutions are of great importance in the use of this material for continuous photographic films, where freedom from specks is absolutely necessary on account of the high magnification to which the film is subjected when thrown upon the screen.

In the manufacture of a suitable paper for this purpose, the Diamond Paper Mills and other manufacturers are obliged to exercise great care in locating their plants, to insure that the water supply is soft and practically free from organic matter, so that the paper may absorb little or no color from percolation through leaf mold and other decaying vegetable matter.

Of the less important processes, the apparatus of R. Schüpphaus and M. White[1] (Figs. 197, 198) consists of a cage, *B*, with a central perforated cylinder, intended to insure the rapid and efficient saturation of the tissue paper used for nitration. The patentees

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[1] U. S. P. 406597, 418237, 1889. E. P. 18683, 1894; abst. J. S. C. I. 1894, **13**, 1010, 1129, 1220; 1897, **16**, 498; Chem. Ztg. Rep. 1896, **20**, 204.

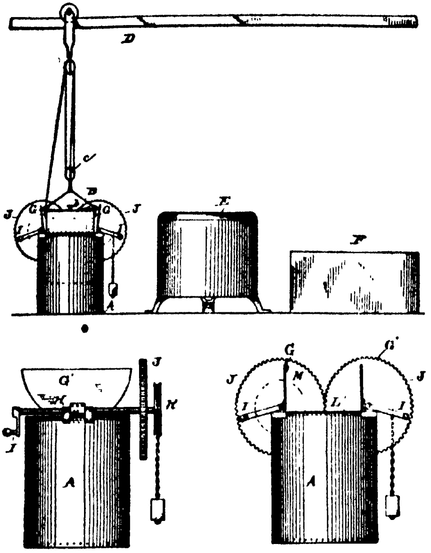

FIG. 197.—SCHUPPHAUS & WHITE METHOD OF PAPER NITRATION

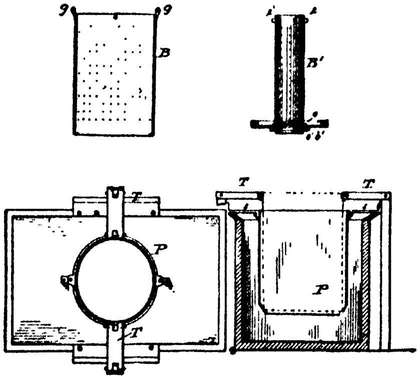

FIG. 198.—SCHÜPPHAUS & WHITE METHOD OF PAPER NITRATION

claim that with their apparatus no stirring is required, which could only be true with nitration at low temperatures, and not with a temperature of 50°–60°. Their method consists in nitrating the paper in the cage *B*, the bottom of which is formed by the flanged plate *c* fastened to the bottom of the internal cylinder *B'*. After nitration the cage goes to the wringer *E*, of which it forms the basket, the acids then being removed. The cage is next taken to the plunge tank *F*, where the paper is removed by simply pulling out the central perforated cylinder *B'*. The lower cut shows the nitrating pot with automatic cover, the plunge tank *F* being shown in section and plan.

The method of G. Mowbray,[1] now chiefly of historical interest, is perhaps the most elaborate process of tissue-paper nitration which has gone beyond the experimental stage, no paper being nitrated by this method at the present day. The paper lengths shown in the various sectional drawings (Figs. 199 and 200) are entirely imaginary, as the paper upon entering the nitrating fluid would immediately fall to the bottom of the recep-

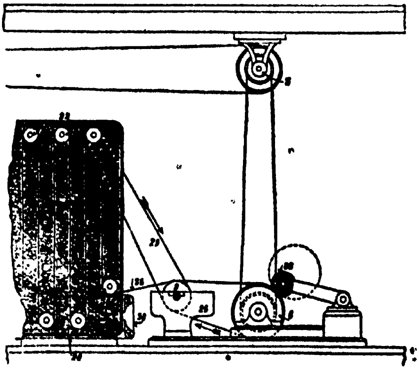

FIG. 199.—MOWBRAY'S PAPER NITRATING APPARATUS

tacle. He allows the paper web to remain in the acid tank for 12 to 20 minutes, then as the first portion is drawn forward a fresh section takes its place. How to maintain the temperature and strength of acid in the nitrating tank is not stated and is one of the important problems. This method was tried commercially at the plant of the American Zylonite Company, at North Adams, Mass., but was shortly after abandoned.

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[1] U. S. P. 350497, 350498, 1886; 434287, 443105, 1890; abst. Chem. Ztg. 1891, **15**, 48; Chem. Tech. Rep. 1890, **29**, II, 145. E. P. 20978, 1890; abst. J. S. C. I. 1891, **10**, 271. D. R. P. 59929, 60595, 1890; abst. Wag. Jahr. 1891, **37**, 431; Zts. ang. Chem. 1892, **5**, 31; Chem. Tech. Rep. 1891, **30**, II, 254; Ber. 1892, **25**, 253. Ital. P. 29266, 1891. J. France has described methods of using cotton cut so fine as to be practically dust, for the preparation of soluble (U. S. P. 420445, 1890) and insoluble (U. S. P. 420446, 1890) nitrocellulose.

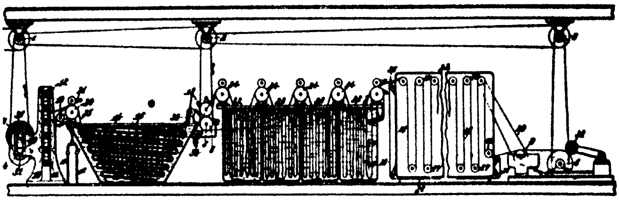

FIG. 200.—MOWBRAY'S PAPER NITRATING APPARATUS

V. Tribouillet and L. de Besauncele Process for Paper Nitration. In this method, the cellulose is first dried at 100°, and is then partially comminuted. The apparatus used for nitration is shown in Fig. 201 and comprizes a nitrating box with hood into which the disintegrated or comminuted cotton is immersed. The nitrating vessel *A* is 7″–8″ deep, and mounted on a bottom cooling jacket, *B*, traversed by a stream of water. To protect the operator from fumes, each unit is surrounded by a glass cover, *V*, which, to say the least, must be inconvenient.

The nitrating mixture is composed of 3 parts sulfuric acid (1.834 sp. gr.) and 2 parts concentrated nitric acid containing nitrous acid in solution, and used at a temperature of 40°–50°. The acids may be economized by employing the bath after re-use, the bath being heated to 30°–35°; but when using spent acid, the material must remain in the nitrating bath for several hours. The nitrocellulose produced is alleged to be especially valuable for the manufacture of celluloid and similar plastics.[1]

A. Claessen has described[2] a method of producing an alcohol-soluble cellulose nitrate, especially suitable for celluloid manufacture, and prepared by acting upon 100 gm. cotton with 3 k. nitrosulfuric acid at 40°-50°. The nitrating mixture containing 19% water (limit 18%-20%), 42% sulfuric acid (limit 35%-46%) and 39% nitric acid (limit 35%-45%) is allowed to act for two hours, the temperature not being permitted to rise above 50°. After nitration, washing with cold water is followed by

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[1] V. Tribouillet and L. de Besauncele, U. S. P. 216474, 1879; abst. J. A. C. S. 1879, **1**, 261. E. P. 5057, 1878. F. P. 126846, 1878; 129890, 1879; Add. June 16, 1880; abst. Mon. Sci. 1880, **22**, 956. Chem. Tech. Rep. 1879, **18**, II, 135. Dingl. Poly. 1880, **235**, 203; abst. Jahr. Chem. 1880, **33**, 1370; Mon. Sci. 1879, **21**, 696; Chem. Centr. 1880, **51**, 334.

[2] D. R. P. 163668, 1904; abst. Mon. Sci. 1906, **65**, 159; Chem. Centr. 1905, **76**, II, 1568; Chem. Ztg. 1905, **29**, 1149; Jahr. Chem. 1905–8, II, 992; Wag. Jahr. 1905, **51**, II, 570; Zts. ang. Chem. 1906, **19**, 204.

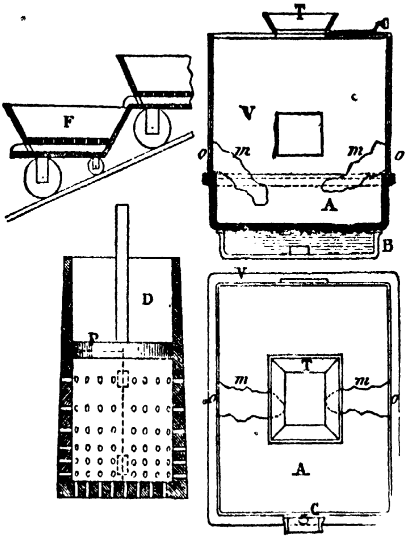

Fig. 201.—The Tribouillet & Besauncele Nitrating Apparatus

reatment with weak soda solution, then with water again and nally dried. The product contains 9.5%-10.5% N, and is said o be readily soluble in 96% alcohol. In polarized light the fibers ppear greenish yellow. To prepare celluloid it is recommended) combine 100 k. of the above cellulose nitrate with colophony 0 k. and 60 k. of 96% alcohol. Instead of colophony, ceresin hich gelatinizes in 96% alcohol may be used.

Hyatt's Paper Nitration Process. The foregoing described iethods have been superseded, at least in the United States, by the process of John W. Hyatt, which, although now thirty years old, is used to-day in essentially the same manner as first brought out by the inventor. With the exception of unimportant modifications and modern refinements in the way of increasing the yield and greater percentage of acid recovery, the process stands to-day alone for the commercial preparation of nitrated tissue paper. So far as the author is aware, the manufacturers of pyroxylin plastics in the United States at the present time use or produce nitrated paper by methods based upon this process of Hyatt.[1] The process is divided into the four steps of "disintegration," "conversion," "desiccation," and "ablution." This method, upon which tissue-paper nitration is at present carried out, is considered of sufficient importance to give in detail, in substantially the words of the inventor:

The first step of the process has for its object the preparation of vegetable fiber for rapid conversion into nitrocellulose, and to this end the improvement consists in taking paper (unsized and uncalendered tissue paper is best) which has been made in sheets, and, preferably, paper made from stock which has been bleached by any of the ordinary processes, and reducing this paper to small flakes; and this is done in practice by taking a roll of such paper, mounting it in frame, and feeding it between rollers and under tension to a cylinder armed with hook-teeth, set close together, which tear the sheet of paper into exceedingly minute shreds or particles ("flakes"), presenting almost as much edge as surface, so that when immersed in the acids they are acted upon almost instantaneously throughout, and converted more uniformly than would otherwise be practicable. This first step of the process is designated "disintegration," to express the reduction of the tissue paper into minute flakes.

To expedite the converting action still further, the second stage consists in preparing the acid bath, which is placed under a shaft carrying on its lower end a stirrer, and rapidly rotating the shaft, so that the stirrer will give the bath a swift swirling motion; and by setting the blades of the stirrer at an angle somewhat similarly to the blades of a propeller, the centrifugal motion of the acids is increased, crowding them up at the side of the vessel and leaving a depression at the center, so that the flakes of paper being fed into the bath are first swept into the vortex of the swirl by centripetal force, and there subjected to the intensified action of the bath, and as the increasing mass of flakes is saturated and immersed it is gradually swept from the center to the side of the vessel, where its motion is slower, leaving the center free for the reception of the fresh flakes, which are constantly fed into the vortex, where they are acted upon on all sides instantaneously. In this way the treatment of a much larger quantity of the paper is effected than the bath would otherwise act upon effectively. This second step of the process is designated "conversion," to express the transition of the disintegrated flakes from their normal condition into that of saturated soluble fiber.

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[1] U. S. P. 210611, 1878. U. S. P. 296967, 297935, 1884; abst. J. A. C. S. 1884, **6**, 204, 207. E. P. 3864, 1881. F. P. 109053, 1875; 123739, 1878; 144726, 1881; abst. Mon. Sci. 1882, **24**, 730. D. R. P. 3392, 5458, 6902, 1878; abst. Dingl. Poly. 1879, **232**, 520; Chem. Tech. Rep. 1879, **18**, I, 291; Wag. Jahr. 1878, **24**, 467. J. Hyatt and F. Pool, U. S. P. 274335, 1883. J. Hyatt, F. Pool, J. Everding, J. Stevens and W. Wood, U. S. P. 299388, 1884; abst. J. A. C. S. 1884, **6**, 249. J. Hyatt, W. Wood and J. Stevens, U. S. P. 296968, 1884; abst. J. A. C. S. 1884, **6**, 204. J. and I. Hyatt, U. S. P. 105338, 1870; Re. 9528, 1874; 10469, 1884; abst. J. A. C. S. 1884, **6**, 204. F. Pool, U. S. P. 306519, 1884; Re. 10650, 1885; 336822, 343850, 1886; abst. J. A. C. S. 1886, **8**, 68, 171.

The quantity of flakes which can be properly fed into the bath, and properly acted upon, as described, having been thoroughly converted, the workman raises the stirrer out of the vessel, which has been resting upon a turntable, and brings under the stirrer another vessel, which meanwhile has been supplied with acids pumped up through pipes, arranged in proper relative position to have the vessel brought under them by the rotation of the turntable. He then lowers the stirrer into this freshly charged vessel, sets it in motion, and feeds in fresh flakes, as before, and when they are converted, again raising the stirrer passes the vessel onward by the turntable.

The next stage of the process is the separation and recovery of the surplus acid from the saturated soluble fiber, and this is effected as follows: Close to the turntable and near to the acid-supply pipes a centrifugal machine is placed, provided with a second perforated rotating removable basket, fitting loosely within the ordinary perforated basket, which latter is mounted upon a vertical shaft, carrying a driving pulley upon its lower end. The acids pass through the perforations in the baskets into the space between the outer basket and the casing, and off through a pipe leading from the bottom of this casing to the reservoir below, from which they may be again pumped up through the supply pipes.

The turntable having brought the vessel containing the acid and converted fiber opposite the centrifugal machine, the vessel is lifted and its contents emptied into the centrifuge which, rotating rapidly, throws out the surplus acid, as is well understood. This third stage is designated "desiccation," to indicate the removal of the surplus acid.

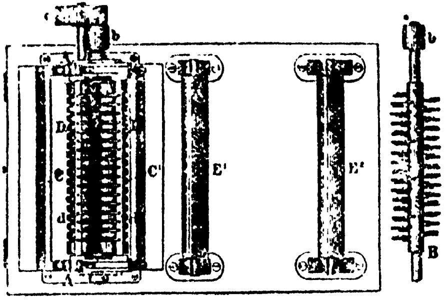

FIG. 202.—HYATT TISSUE-PAPER NITRATOR. TOP VIEW OF DISINTEGRATING APPARATUS

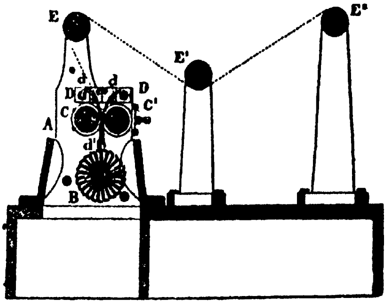

FIG. 203.—HYATT TISSUE-PAPER NITRATOR. VERTICAL LONGITUDINAL SECTION THROUGH FIG. 202

The next stage is to wash out the acids left in the desiccated fiber after the operation of the whizzer; and to this end a washing vat is arranged, supplied with water, and having an overflow near the top, and an inclined table extending from the whizzer to the edge of the vat, so that by lifting the removable basket out of the whizzer with suitable lifting-hooks the desiccated fiber is dumped on the table and slides down into the washing-vat, where it is stirred and thoroughly washed in the constantly changing water until the acids are throughly removed. This fourth stage is designated "ablution," to express the transition of the nitrocellulose from the condition of desiccation to the condition of hydrated soluble fiber. From this vat the hydrated soluble fiber may be transferred to another whizzer, which will remove the surplus water, or to a beating-engine, and ground into pulp.

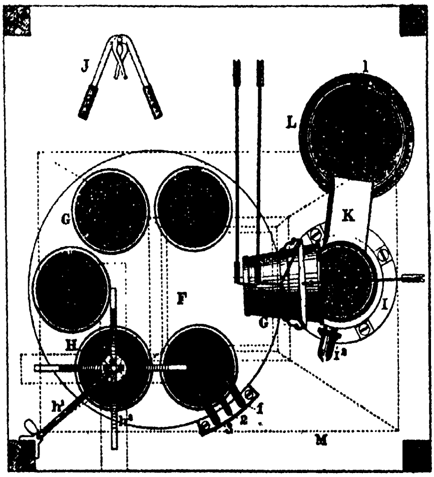

FIG. 204.—HYATT TISSUE-PAPER NITRATING APPARATUS. PLAN VIEW SHOWING CONVERTERS

A hood or canopy is provided extending over the entire apparatus, and having an induced upward draft through it, whereby the fumes from the acids are not only prevented from becoming diffused throughout the room, but are so rapidly carried off through the hood as to greatly relieve the workmen immediately about the apparatus from the distress incident to the use of such acids in open vessels.

The converting vessels are also provided with lugs above and below the center of gravity, and rig-lifting apparatus at the proper points for elevating and tilting the converting vessels to empty them into the whizzer; and by the use of these devices and of a suitable lifting-hook for raising the removable basket from the whizzer, the process is conducted with very little occasion to touch the vessels with the hands.

In the drawings Fig. 202 is a plan or top view of the disintegrating apparatus; Fig. 203, a vertical longitudinal section through the same; Fig. 204, a plan view, showing the general arrangement of the converting apparatus; and Fig. 205, a side view, in elevation, of the same.[1]

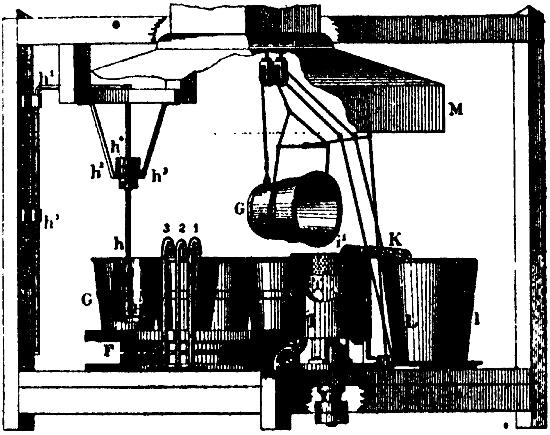

FIG. 205.—HYATT TISSUE-PAPER NITRATOR. SIDE VIEW OF FIG. 204

It has been said that when Hyatt utilized the relation of

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[1] The disintegrating apparatus consists of a frame supporting a pair of housings, *A*, with bearings below for the shaft of the disintegrator *B*, and bearings in adjustable boxes above for the grooved feed-rollers, *CC'*, a driving-pulley, *c*, being mounted on the projecting end of the shaft of the feed-roller, *C*, which roller rotates the feed-roller, C_1, by frictional contact. The housings also support a transverse frame, *D*, in which guide-teeth, *d*, of wire, are so arranged that each of them shall take into one of the grooves of the feed-rollers.

The guide-teeth, which fit in the grooves of the roller, *C*, extend down camphor to pyroxylin he laid the foundation for an art, and when he devized a satisfactory process of paper nitration whereby

below the feed-rollers, and are secured to and support the guide-bar, d', parallel with the roller and immediately above the teeth of the disintegrator, in line with the line of contact of the feed-rolls.

The teeth which fit in the grooves of the roller C' are slightly curved at their lower ends, so as to turn away from the bar d', and the lower points of these teeth are about in line with the lower edge of the guide-bar.

As the feed-rollers are rotated the paper is carried down between them and between the teeth, in such a manner that while the teeth in the roller C' permit the paper after it passes below them to turn toward the knives, the guide bar d' sustains it against the action of the knives and holds it smooth throughout its entire width, so that it is uniformly fed under the tension of the rollers and presented to and acted upon by the teeth of the disintegrator and reduced to substantially uniform flakes, instead of being irregularly torn and wadded.

The disintegrator B consists of a number of hook-teeth or knives arranged close together in spiral lines around and upon its shaft. The elements which will determine the size of the flakes are a given number of teeth and a given rate of speed in the disintegrator, and a relatively slower rate of speed in the feed rollers; but it was not found desirable to reduce the paper to flakes of less size than, say, one-sixteenth of an inch.

The revolution of the disintegrator is in a direction opposite to that of the driven feed-roller, and is imparted by a pulley, b, on the projecting end of the disintegrator shaft.

The paper is supplied to the disintegrator from a roller, E^2, and passes under a roller, E^1, and over a roller, E, down to and between the feed-rollers CC^1.

The flakes fall into a receptacle below the disintegrator, from which they are removed as required.

The converting apparatus is arranged as shown in the figures, and comprises first, a turntable, F, mounted on spherical balls or other suitable suspension and having such diameter as will accommodate a series of the converting vessels G. At a proper point supply pipes 1, 2, 3, leading from the acid reservoirs below, have their spouts curved over, so that one of the vessels, G, standing upon the turntable, may, by the rotation of the table, be brought under the spouts and charged with acids by the action of a pump. The further rotation of the turntable then moves the charged vessel from the spouts around underneath the stirrer H, which is supported above the turntable, so that the charged vessel on the turntable will stand under it centrally. This stirrer is composed of a series of short blades, set or bent at a slight inclination to their shaft, so that they will induce a swirling motion in the acid bath, and attached to the lower end of a vertical shaft, h, which can be raised high enough above the turntable for the vessel to be placed under or removed from beneath it, and lowered so as to rotate in the vessel near the bottom. This raising and lowering of the stirrer is effected through a bent rod, h^1, connected with the upper end of the shaft h. The shaft h of the stirrer passes through a depending bracket, h^2, and is provided with a loose pulley and a fast pulley h^3,h^4, through which, when the stirrer is lowered so that the pulleys are brought together, the stirrer is rotated by a belt, the motion being stopped, however, when the shaft is raised and the fast pulley h^4 removed from the action of the belt. A pin passing through the rod h^1 and resting upon a bracket, h^5, sustains the stirrer when raised. It will, of course, be understood that the blades of the stirrer and so much of its shaft as is liable to be reached by the acids should be made of or covered with copper or other metal or composition which will resist the corrosive action of the acids, and the same precaution should be observed in protect-transparent objects hitherto unattainable could be produced in large quantities and including the imitations of ivory, mosaics, coral, and amber, he laid the foundation for a "fine" art. It is understood that the proportions of nitrating acids found satisfactory by Hyatt are in the ratio of 50 cc. nitric (sp. gr. 1.47), 100 cc. nitric (sp. gr. 1.36), 100 cc. sulfuric (sp. gr. 1.84) and 18 gm. finely shredded tissue paper, immersed at a temperature of 55°

ing all the surfaces of the apparatus liable to be attacked and impaired by the acids.

The stirrer being lowered into the charged vessel *G* and set in motion and the acids having been brought to the proper swirl, the flakes of the disintegrated paper are fed into the vessel at or near the center or vortex of the swirl, and subjected to the action of the bath, this stirring operation being continued until, by the action of the acids, the flakes have been thoroughly converted into nitrocellulose. The flakes fed into the center or vortex are, by the operation of the stirrer blades, thrown outward toward the side of the vessel, and their place is supplied by fresh flakes fed in at the center until the thickness of the mass indicates the limit of the saturating capacity of the bath, when the shaft of the stirrer is raised and the turntable rotated, carrying the vessel from underneath the stirrer round opposite a whizzer or centrifugal machine, consisting of the case *I*, firmly secured in position, the perforated rotating basket, *i*, mounted upon the upper end of the vertical shaft, by which it is rotated through a pulley on the lower end of the shaft, and the removable perforated rotating basket, i^1, fitting loosely within the basket *i*.

To transfer the converted flakes from the vessel *G* a tackle is rigged between the turntable and the whizzer, with three hooks, two on one rope, to take into the lugs or eyes on the sides of the vessel, and thereby lift the vessel, and one on the other rope, which takes into the lug or eye near the bottom of the vessel to tilt it when raised; and on the opposite side of the whizzer a line is provided, running through the eye to the lifting tackle, so as to draw the raised vessel into proper position to be tilted and emptied into the removable basket of the whizzer. The whizzer meanwhile having been duly set in motion, the surplus acid is rapidly expelled from the converted flakes, and passes down between the outer basket *i* and the case of the whizzer to a pipe, i^2, which conducts it to the cistern or reservoir, from which it may be again pumped up through the supply pipes 1, 2, 3. When the action of the whizzer is completed and the converted flakes freed from the surplus acid, the removable basket i^1 is lifted out by means of a pair of internal lifting hooks, *J*, 4, and its contents dumped upon the inclined table *K*, and into the washing vat *L* which is supplied with water, and the converted flakes are stirred and washed therein, under a constant circulation of water, supplied in any suitable manner and passing off through the overflow *l* near the top of the vat. From this vat the washed mass is removed for further treatment not pertaining to this process, which is concluded with this condition of the hydrated soluble fiber.

It will be observed that the diameter of the turntable is such as to allow space for a series of the converting vessels *G*, the relative position of which is such that while one in is readiness to be lifted and its contents dumped into the vessel, another is being charged with acid, and a third is beneath the stirrer, while between the one under the stirrer and the one at the whizzer there is room for several others, so that there may be always a series of vessels that have passed the stirrer, ready for being dumped into the whizzer and passed again under the supply pipes, and the operation may be thus carried on without any intervals between the stages.

for one-half to one hour, the paper increasing in weight by about 40% during the nitration. The size of the individual pieces is a matter of adjustment of the shredding machine, that produced to-day being about $^1/_2$ to 1 inch.[1] Ash determinations made by the author on this paper gave results of 0.08–0.12%.

The Swan Apparatus for Paper Nitration. The invention

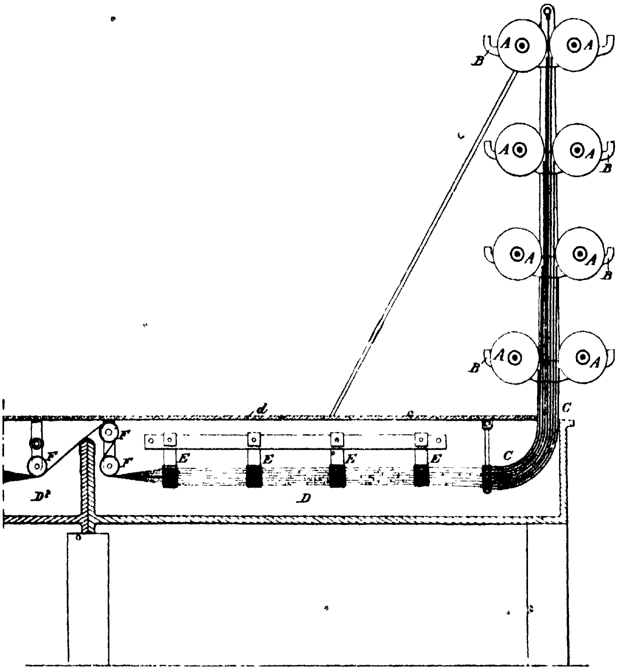

FIG. 206.—SWAN APPARATUS FOR PAPER NITRATION

of J. Swan[2] has for its object the manufacture of guncotton or similar nitrocellulose in a practically continuous manner arranged so as to minimize manual labor, diminish irregularity in manufacture, and decrease exposure of the workmen to deleterious fumes. The process is executed by means of the apparatus shown in Figs. 206 and 207, in which the latter illustration is a continuation of the machine shown in the former. The paper or other form of cellulose is carried on rollers *A*, thence passing by guides *C* to the first nitrating tank *D*, through which the sheets pass and are separated by guides *E*. They next pass over rollers *F* to the next tank D^2, where they are similarly separated by guides E^2, and so on through other tanks if desired. They leave the last tank between squeezing rollers *G* which deliver them to a table, *H*, where they are cut into strips by rotary cutters *I* and fall into a washing tank, /. This tank has agitators *K* which wash the nitrated cellulose and pass it over the partition *L* upon the tray *m*. from which the water passes by the passage *n*. The various rollers, knives and agitators are actuated by suitable driving gear.

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[1] Analyses made by the author of that grade of paper pyroxylin most suitable for lacquers gave nitrogen 11.0–11.2%, ash 1.0%, KI starch test at 65°, about 15 minutes; temperature of ignition 170°–175°.

[2] E. P. 21729, 1894; abst. Arms and Explos. 1896, **4**, 46; J. S. C. I. 1895, **14**, 1062.

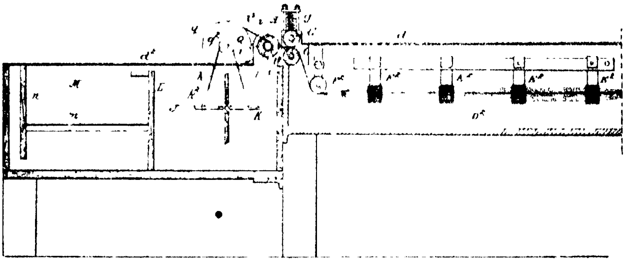

FIG 207—SWAN APPARATUS FOR PAPER NITRATION

Other Methods of Paper Nitration. In addition to the processes previously described, several other methods have been proposed and devices perfected, which merit attention. The method of the Celluloid Company at Stains near Paris, employs paper made from cotton or linen, weighing about 50 gm. per sq. cm., which is immersed in the usual manner in concentrated nitric acid to which has been added a relatively small proportion of sulfuric acid, the nitropaper after esterification, being drained, washed with cold and then hot water, treated with dilute aqueous ammonia to complete the neutralization, and finally dried.

A. Müller-Jacobs[1] has described a method whereby the

[1] E. P. 27162, 1904; abst. J. S. C. I. 1905, **24**, 250. D. R. P. 174930;

cellulose is nitrated, washed, stabilized and dried in endless sheets, which afterwards are transformed into explosives by impregnation with oxidizing agents. In the S. Emmens process,[1] *paper or paper pulp is nitrated in the usual bath, the nitropaper being afterwards steeped in a weak aqueous solution of ammonium carbonate until entirely neutral.*

According to V. Pallotti,[2] *a superior smokeless powder called by him "Nivea," results when paper is immersed into a solution* of 3 parts H_2SO_4 of 66° Bé., and 1 part HNO_3 of 40° Bé., and the resulting nitrated paper combined with barium nitrate, potassium nitrate and sodium carbonate to a homogeneous paste. The J. Clouet method[3] employs 5 parts of sulfuric acid and 2 parts nitric acid to each part of tissue paper, all being by weight. The E. Zettnow collodion[4] is prepared from nitrated paper.

More recently a process has been brought forth by M. Delpy[5] for the nitration of tissue paper in sheets centrifugally, the essence of which consists in placing one or two reels of paper above the nitrating basket of the centrifugal machine, which are unwound by the force of jets of the nitrating acid directed obliquely against one or both surfaces of the paper, something similar to a "draw" shot in billiards. The nitrating fluid is directed at an inclined angle against the moving strip of paper. The details of the apparatus are shown in Fig. 208.

Selwig and Lange have devized an arrangement for feeding paper into the nitrating vessels in the manufacture of nitrocellulose,[6] the apparatus consisting of a vertical stem suspended from a traveling carriage, which can be adjusted over any of the nitrating vessels. At the lower end of the stem is situated a reel of paper, the paper from which passes over a guide roll, and

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abst. Wag. Jahr. 1906, **52**, I, 481; Chem. Centr. 1906, **77**, II, 1151; C. A. 1907, **1**, 952. U. S. P. 777125, 1904; abst. J. S. C. I. 1905, **24**, 44; Tech. Chem. Jahr. 1904, **27**, 199. F. P. 348807, 1904; abst. Chem. Zts. 1905, **4**, 184; Mon. Sci. 1906, **65**, 60.

[1] E. P. 3852, 1890; abst. J. S. C. I. 1891, **10**, 484.

[2] Ital. P. 34559, 1893.

[3] Bull. Soc. Rouen 1877, **5**, 36; abst. Dingl. Poly. 1877, **226**, 646; Jahr. Chem. 1877, **30**, 1223.

[4] Pogg. Ann. 1871, **144**, 310; abst. Jahr. Chem. 1871, **24**, 1123; Amer. Chemist, 1872, **2**, 354; Poly. Centr. 1872, **38**, 191; J. C. S. 1872, **25**, 337.

[5] F. P. 458558, 1913; D. R. P. 256788, 1912; abst. J. S. C. I. 1913, **32**, 1063; C. A. 1913, **7**, 2116; Chem. Zentr. 1913, **84**, I, 1080; Chem. Ztg. Rep. 1913, **37**, 144; Wag. Jahr. 1913, **59**, I, 438.

[6] F. P. 409220, 1909; abst. J. S. C. I. 1910, **29**, 751; Mon. Sci. 1910, **73**, 295.

between a pair of guide rolls also carried between the stem. The drawing rolls are operated by means of a belt driven by an electric motor mounted at the upper end of the vertical stem. An oscillatory motion may be imparted to the stem if desired.

Masselon, Roberts and Cilliard have described an arrangement for the nitration of 500 kilos of paper per 10-hour day,[1] consisting of a series of pots arranged in a circle round one or more centrifugals. The nitration period per pot is given as 50 minutes, of which the unwinding of the paper consumes 10, the nitration 30, and the hydroextraction 10 minutes. Operating in this manner with a charge of 5 kilos per pot, 60 kilos of paper may be esterified per day. The pots are 800 mm. diameter and 900 mm. high, and are provided at their base with a tap. The layout of a single unit comprizes 8 nitrating pots, two centrally located centrifugals, and two vats each for preliminary washing

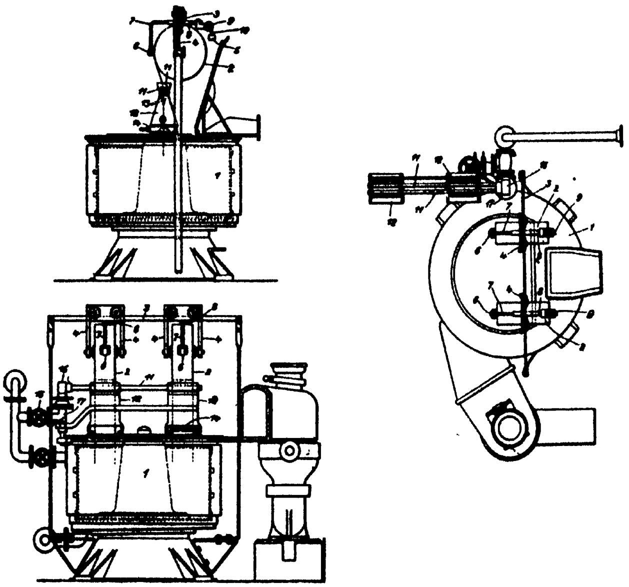

FIG. 208.—DELPY PAPER NITRATION APPARATUS

and for washing proper, each vat being 1.5 m. long, 1 m. wide and 0.9 m. high for the two former, and 5 m., 2 m., and 0.9 m., respectively, for the dimensions of the latter vats. Where the battery system of nitration is in use, a single paper unwinding apparatus is employed, which includes a light framework attached to the ceiling of the nitrating house, by means of a pivot placed above the pots. In addition, a unit as above contains 5 tanks each of 12,000 liters capacity for the storage of fresh and spent acid, one or two of the tanks being jacketed to allow of cooling or heating the nitrating mixtures. An exhaust fan and air compressor with its store of compressed air is also provided.

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[1] "Celluloid," 1912, 63.

Manufacture of Nitrolignin. The preparation of wood pulp for nitration has been detailed on pages 293-324, and the historical aspects of the development of the nitrolignins has been touched upon on pages 1808-1815. The first successful attempt to nitrate lignin on a commercial scale was probably made by E. Schultze in 1864 in England, where manufacture has been carried on uninterruptedly until the present time.

In sporting and bulk small arms powders nitrolignin is extensively used in the United States, as well as in England and on the Continent, and while the percentage yield on nitration is inferior as compared to the nitration of cotton under similar conditions, the initial cost of the raw material is also lower. One factor which undoubtedly militated against the wider use of the nitrated lignocelluloses has been the difficulty of purifying the lignin before esterification, and also the unusually large losses of product in the various processes of washing incident to stabilization.

Difficulty in purification of the raw material is necessarily reflected in a corresponding difficulty in rendering the product sufficiently stable. This fact, perhaps more than any other, has, up to the present, deterred Governmental adoption of nitrolignin as an official propellent powder for army and navy purposes, all official powders—so far as aware—at the present time being manufactured, are produced from some form of cotton cellulose.

At the present time when solvents are so expensive, efforts are made to produce nitrocelluloses for use in the peaceful arts of minimum viscosity in order to conserve solvents. As is well known, lignin gives less viscous nitrates than cotton—a point in favor of the former. During the recent war immense amounts of lignin were esterified for smokeless powder manufacture in Germany, and lignin also—after purification by solution in concentrated HCl and precipitation (see page 92)—were utilized for acetation in the preparation of dope for airplane wing coating.

Apparently insufficient attention has been given to the selection of the wood pulp for nitration, and the influence of the physical condition of the lignin upon the finished nitrated product. Whereas an immense amount of painstaking investigation has been expended upon the selection and preparation of cellulose (cotton) for nitration, so far as published results would indicate, there is a paucity of information upon the subject of lignin purification and selection, and the bearing of the physical constants of the purified wood pulp upon the stability of the finished nitrated wood.

In the method as originally evolved by E. Schultze, the wood was cut into small grains somewhat resembling coarse sawdust, boiled several times with dilute sodium carbonate solution in order to saponify resinous constituents, then washed to remove alkali, carefully bleached, and afterwards treated with nitric and sulfuric acids. The neutralized nitrolignin was usually incorporated with a solution of barium or other nitrate to supply the deficiency in oxygen for ideal combustion, carefully dried and granulated. Later improvements were along the lines of decreasing the dust from the grinding operations of mixing with inorganic nitrates, by means of hydraulic pressure, the cake formed being then disintegrated and broken up into grains of suitable size by means of crushing rollers. Granulation was usually induced by moistening the impalpable powder and revolving in barrels, the mass being afterwards sifted in order to obtain grains of the desired size.

The method of the Smokeless Powder Co. in England for the preparation of nitrolignin was to take wood pulp such as is used in the manufacture of paper by the soda or sulfite method (the latter being generally adopted for the manufacture of nitrocellulose because it is softer, more fluffy and porous, and hence more readily penetrated by the nitrating acids than soda pulp). This material is received from the paper mills in sheets or rolls about 0.05 inch thick, and tear it by hand or mechanically into small pieces of about two square inches area. The material was then passed through a disintegrator to open up the compacted fibers and make the mass more absorptive for acids. The division into small pieces, and also the opening up of the fibers is done in one operation by passing through a stoutly built machine consisting of a revolving cylinder on which are mounted projections, the revolving projections passing between similar immoval ones attached to a stationary arc concentric to the moving cylinder.

The operation gives rise to a considerable amount of dust, on account of the comparatively short length of the fibers. The wood pulp is dried before nitration in a manner similar to that described for cotton (see pp. 634–642). For the manufacture of nitrolignin the pot, pan and centrifugal methods as previously described have been used.

In the pot method of nitration which was carried out for many years at the plant of the Smokeless Powder Co., the pots were made of stoneware, and were about 12 in. in diameter and 8 in. deep, the acids employed consisting of the usual mixture of three parts of strong sulfuric acid to one part of concentrated nitric acid. Into each pot 15 lbs. of mixed acid was run, and the pots placed in pits through which cold water circulated. One pound of wood pulp was added to the acid charge in each pot, a little at a time, a workman immersing the pulp by means of a long iron rod, at the end of which is affixed a perforated disc about 4 inches in diameter.

On account of the small weight of acids used relative to the cellulose the temperature was liable to abnormal rise, and under the most favorable conditions, the nitration was usually accompanied by considerable fumes. The wood pulp was allowed to remain in the acids 4 to 6 hours, and then the contents of the pots were emptied into a centrifugal, the acids extracted, and the nitrocellulose then removed from the centrifugal and thrown into drowning tanks. The nitrocellulose produced was quite soluble in acetone, had a nitrogen content of about 12.8%, and a solubility in ether-alcohol close to 20%. After the addition of nitric acid the spent acids were again used, this time to produce a nitrocellulose of about 11.5% nitrogen. The acids extracted from the nitration of this latter product were denitrated and concentrated.

As in the nitration of cotton, the pot method may be considered as a process in which the ratio of weight of acids to cellulose is comparatively small.

The process of purification adopted for nitro-wood pulp is generally on the same lines as for nitrocotton, although the Smokeless Powder Co. used heavy edge-runners in place of rag-engines or beaters for breaking up the nitrated fibers into pulp, a method covered by a patent granted to S. Mackie in 1872.[1]

The author in July, 1919 inspected the factory of the Westfalische Anhaltische Sprengstoff A. G. at Troisdorf, Germany, where nitrolignin was being manufactured. In the method employed the wood pulp in rolls similar to that of paper was first dried by being placed in a room at 45°–60° for several weeks if possible, and until the moisture content had been reduced to under 3%, when it was passed through a disintegrating machine which shredded it into unequal pieces of about one square inch area. From the disintegrator it was immediately weighed into batches, and, after cooling, placed in a Selwig & Lange nitrating centrifugal with acid circulation and subjected to a 20-minute nitration, the basket being rotated at a speed of 35 to 45 r. p. m. From the nitrator the material was immediately plunged into a large bulk of cold water, stirred by hand at intervals for a half to one hour, then submitted to a preliminary boiling in wooden tubs without stirring device. The boiling operation consisted of a series of treatments with hot water until the free acid had substantially all been removed.

The acid boil was followed by a beating treatment in hollanders similar to those already described, except that due to the softness of the fiber as compared with cotton, disintegration takes place much more readily, and the period of pulping is correspondingly reduced. From the pulper by means of pumps, the mass is transferred to the poachers where blending and further purification ensues by means of a series of washings, during which the contents of the poacher is mechanically agitated. The now sufficiently purified nitrated lignin is hydroextracted, and either alcohol-dehydrated centrifugally or directly mixed with alcohol, camphor and the other ingredients entering into the manufacture of pyroxylin plastics similar to celluloid.

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[1] E. P. 2693, 1872; abst. Ber. 1874, **7**, 741; Dingl. Poly. 1874, **213**, 174; Poly. Centr. 1874, **40**, 789; Bayr. Ind. Gewerbl. 1874, 276; Chem. Tech. Mitth. 1874–1875, 218.

C. Claessen[1] prepares cellulose for nitration by subjecting the latter to a mercerization treatment by means of sodium hydroxide, or[2] the dried cellulose pulp is rolled and pressed, and the compressed material reduced to a fine state of subdivision by a suitable woodworking machine. A uniform porous substance is said to be thus obtained, which can be nitrated in the usual manner.

O. Kress and S. Wells[3] have described the preparation of pulp from cotton linters. The explosive of G. Peters and M. Lindsley,[4] especially applicable to blasting, is composed of 10% nitrated wood fiber with ammonium nitrate, nitrobenzene, $CaCO_3$ and NaCl. The development of nitrolignin powders is treated in detail in Volume VII of this series.

Efficiency of Various Nitration Methods. The relative efficiency of various classes of nitration methods depends upon a number of not clearly defined factors, and in order to be able to arrive at tangible and intelligible comparisons, labor costs, prices of raw materials and other economic conditions are important factors for consideration, so as to arrive at generalizations fruitful for discussion.

Inasmuch as, roughly speaking, one-third of the cost of manufacture of nitrocellulose is represented by the acid consumed or lost in nitration, of which, only about one-half of the monetary value of the acid combines with the cellulose, it is obvious that here is a most important field for attempting to reduce costs of production, and also of differentiating between the efficiency of one general process over another. The acid losses in nitration are either "chemical" or "mechanical," the former representing nitrogen in combination with the cellulose, and the latter indicating the acid adhering to the nitrated cellulose after the acid wring, and hence not recovered. In endeavoring to base relative nitrating efficiencies, it must be remembered that the higher the cellulose nitrate produced, the greater the nitric acid consumed in combination. For instance, nitrocellulose for celluloid manufacture contains about 10.7% N only, and in producing 100 lbs. of such a cellulose nitrate, 48.2 lbs. of absolute nitric acid is used as nitrogen. A nitric ester of 12% N such as is used in the preparation of pyroxylin lacquers and bronzing solutions, requires 54 lbs. HNO_3 as N.

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[1] D. R. P. 298418, 1915; abst. J. S. C. I. 1920, **39**, 469-A. See Arms and Expl. 1896, **4**, 126.

[2] D. R. P. 300069, 1915; abst. J. S. C. I. 1920, **39**, 429-A.

[3] Paper, 1920, **26**, 320; abst. C. A. 1920, **14**, 2082.

[4] U. S. P. 994273, 1911; abst. C. A. 1911, **5**, 2557; Mon. Sci. 1912, **77**, 32; Chem. Ztg. Rep. 1911, **35**, 550; J. S. C. I. 1911, **30**, 926.

Other losses being designated as mechanical, it is evident that the major mechanical loss is in the quantity of acid adhering to the nitrated cotton, this amount being influenced by the physical condition of the nitrocellulose as to whether soft, hard, porous or spongy, and to the construction of the number, spacing and diameter of the holes in the wringing basket as well as the time and speed of wringing. In the ordinary centrifugalization of spent acid, the nitrocellulose retains about its own weight of acid, which for purposes of calculation may be considered as of the same strength as the extracted acids, and as has been mentioned, are lost in the wash waters of the drowning tank.

The extracted acids of the pot, tank and centrifugal methods may be revivified, so that with these methods there is seldom need to recover by denitration and concentration. On the other hand, with the Abel method, the extracted acids are too weak for profitable fortification, and must be recovered by concentration. Similarly with the displacement process, there is a loss of acids that are too weak for concentration, and in addition, there is an amount of acid too weak for recuperation, but which must be denitrated and distilled. The amount of such acid in this process depends primarily on the gravity at which the cutoff from recoverable to waste acid is taken.

Careful factory experimentations have indicated that there is a direct relation between the total quantity of acid retained in the nitrocellulose as such after wringing, and the nitrogen content, the higher the nitrogen in the nitrocellulose, the less acid is physically retained upon wringing. The probable explanation of the above is undoubtedly in the texture of the various nitrocelluloses, and their comparative receptivity for fluids. Pyroxylins of low nitrogen content are usually spongy and soft to the feel, in contradistinction to the hard feeling guncottons. The more gelatinous the nitrocotton, the greater weight of acid it is capable of mechanically retaining. An additional significant fact has been observed, viz., that due to this difference in absorptive power for waste acid, usually the higher nitrogen nitrocottons are a trifle less expensive to produce as compared with those cellulose nitrates of 10.7%–10.9% nitrogen.

There is no doubt but what *fluffy* or *pilled* cotton fiber causes a smaller amount of acid to be retained than *matted* fiber, although the latter, while packing more closely in the wringing basket, yet is sufficiently non-gelatinous to readily permit the removal of the acid, and in a much shorter period of wringing.

The method of wringing exerts an important effect upon the amount of acid recoverable, and is influenced by the (1) peripheral speed of the wringer, (2) the period of wringing, which is adjusted to the type of nitrocotton produced, and is continued until the power required is equal to or less than the value of acid obtained; (3) the size, number, and smoothness of the wringer basket perforations. If the perforations are too few, a longer time is required; if too large, loss of nitrocellulose takes place; if too rough, they become readily stopped up, and the removal of acid is correspondingly impeded and diminished.

A point of importance, secondary only to the question of acid retention by nitrocellulose, is the loss of acid by fumes. In this, the displacement process is the superior with the minimum loss, *fuming off* being unknown in this method of cotton nitration. In centrifugal nitration with continuous acid circulation there is probably a lower loss from fumes than in the pot or hand nitration processes.

The quantity of fumes normally evolved in any nitration operation is controlled by the factors of nitration temperature, duration of esterification, method and speed of agitation (if any), variety and physical condition of the cellulose being esterified, and the percentage of nitric acid in the mixture. New acid baths fume less, as a general thing, than baths made from acid once or several times used. Diminished agitation of the cotton causes an increase in fumes evolved. High nitric nitrating mixtures evolve fumes more copiously than those nitrating mixtures low in nitric. Moisture in the cellulose is also a factor, since moisture raises the temperature of the nitrating bath and increases fume evolution.

Whereas in the Abel method, or those methods of hand dipping similar to that of Abel, the arduous work made the labor charges high, while, owing to the small proportion of acid left after squeezing, there were frequent decompositions in the pots with heavy evolution of nitrous fumes, and consequent loss of material, i. e., a diminished yield of finished product. The maintenance charges were also considerable, but the long steeping in a small proportion of acid of low nitric acid content had the advantage that the resulting waste acid had a very low percentage of HNO_3, and the consequent loss of this comparatively costly material in the drowning operation was therefore kept down to a minimum.

The Nobel's Explosives Co. Ardeer method was a considerable advance on the Abel method, inasmuch as the nitration was carried out in one stage and with large units, less labor was required and the operation developed less fumes. The substitution of iron for earthenware pots materially reduced maintenance charges due to decreased breakage, while by keeping the percentage of nitric acid in the mixed acid low, and conducting a suitably long steeping, the main points of advantage of the Abel method were still retained.

In the nitrating centrifugal method the cost of conveying the pots or tanks to the centrifugal is saved, and there may be some advantage from the slow circulation of the acid during nitration, but the wear and tear on the centrifugals is heavy, maintenance charges are high, and in order to obviate employing a prohibitive number of wringers, the time of steeping must be short thus necessitating a high percentage of nitric acid in the mixed acid.

The loss of nitric acid on drowning is, therefore, considerable, and this is accentuated by the very high proportion of mixed acid which must be used in order to fill up the space between the wringer basket and the enclosing casing, about 40% of the total being required for this purpose. In those methods in which centrifugals are required to recover the waste acid, and as the proportion of the latter which is retained by the nitrocotton after whizzing cannot be reduced much below one part of acid per part of nitrocotton (both by weight), there is considerable loss on drowning. While it is true that the proportion of nitric acid retained by the nitrocotton may be reduced by spraying the nitrocotton while still revolving in the basket with sulfuric acid as detailed elsewhere in this chapter, there are certain manipulative disadvantages encountered in this method of treatment.

As no centrifugals or drowning tanks are required in the displacement method, and the charges for power and water are much reduced, it follows that considerably less labor is necessary, there is less loss by decomposition, and the maintenance charges are lighter. A further advantage of this process is that the nitrocotton is more easily stabilized, doubtless due to the hydrolytic action of the hot zone of dilute acid, to which the nitrocotton is exposed during the displacement. One disadvantage however, attached to this method is that a large proportion of weak waste acid is produced which has to be recovered by redistillation. In general, however, this method compares favorably with the other methods as to the cost of manufacture. During the past war, especially in Great Britain, this method was carried out in many factories by female labor alone, i. e., at Gretna.

In addition to the nitrating conditions, the general efficiency of a nitrating process, or rather the relative efficiency of a given process as carried out at a particular factory, depends upon the facilities available for the treatment of the waste acid, and this again, is dependent upon the output of the plant in a given period. In every case where the recovery is efficient there will be produced more waste acid than is required for fortification purposes into nitrating acid again to maintain the output of nitrocotton of desired acid content in nitrogen, and it will be necessary to recover the nitric and sulfuric acids from the remainder by distillation and concentration.

The proportion which can be economically again revivified depends upon the degree of concentration of the fresh acids used. In the early days of the art ordinary sulfuric acid alone was available for this purpose, but the present employment of oleum has considerably increased the proportion which can be recovered with profit.

From the above points it will be readily seen that a comprehensive and accurate statement of the superiority or inferiority of one process over another is difficult, unless a large number of factors are taken into intelligent consideration, and comparisons are based upon a particular type of nitrocotton to be produced at a stated temperature in a nitrating bath of pre-determined composition.

The following table of the principal data in connection with the comparison of the four general processes of nitration previously described, is given by Marshall:

Details of the Process	Waltham Abbey Abel	Ardeer Direct Dipping	Dartford Nitrating Centrifugal	Waltham Abbey Displacement
Acids, Analysis:				
H_2SO_4	74 0	75 0	69 35	70 5
HNO_3	18 0	15.75	23 15	21.0
HNO_2	0.6	1 3	.	0.6
H_2O	7.4	7.95	7 5	7.9
Quantity, lbs.	13 75	127	800-1100	650
Cotton waste, lbs.	1¼	4½	16-24	20
Acid per lb. cotton	11.0	28.2	50 0	32.5
Time of nitration, hours	12	12	1	2½
Yield on dry cotton, %	164	159	160	170
Output per man per week, lb	458	1112	3000	1742
			(Approximately)	

In a summary issued by the British Government, the following figures are compiled as to the materials required for one ton (2200 lbs.) of nitrocellulose as made during the entire year 1917 at three of H. M. Explosives Factories:

TABLE CXLVI.—MATERIALS REQUIRED FOR ONE TON OF NITROCELLULOSE

	Normal Basis				Ultimate Basis			
	Cotton Waste		Nitric Acid	Sulfuric Acid	Cotton Waste		Sodium Nitrate	Sulfuric Acid
	Gross	Net			Gross	Net		
Gretna	0 700	0 644	0 808	0 527	0.688	0 619	1.210	1.763
Queen'sFerry	0 665	0 614	0 814	0 585	0 672	0 617	1.073	1.484
Pembrey	0 706	0 639	0 907	0 967	0 684	0.626	1 157	1.781
Average	0 690	0 632	0 843	0 693	0 681	0 621	1.147	1.676

Preliminary Washing of Nitrated Cellulose. The first operation after nitration by hand, pot or centrifugal, is the process of quickly eliminating the bulk of acid adhering mechanically to the nitrated cellulose, and this operation is conducted with maximum speed. Guncotton, previous to the first washing, is exceedingly easily inclined to autocombustion, and this reaction is accompanied by a violent evolution of acid vapor, followed by a total destruction of the nitrated product. This phenomenon is caused by the acid residues remaining in the capillary filaments of the nitrocotton, and which are not removed by the centrifugal wringing.

It is, therefore, imperative to remove the nitrated cotton from the influence of the atmosphere as quickly as possible by plunging it into a large bulk of cold water and stirring until the product is uniformly disseminated and diluted by the mass of water. This operation, technically known as "drowning" or "sousing," is designed merely to dilute the adhering nitrating acid as quickly as possible, and reduce the temperature of the mass.

Where it is desired to automatically transport the nitrated cotton from the centrifugals to the wash-house, the hydraulic guncotton conveyor of Selwig & Lange, as shown in Fig. 209, may be used. It is erected close to the nitrating centrifugal[1] and consists primarily of an aluminium or earthenware funnel 250 mm. wide, into which water enters through an opening below the upper rim in sufficient quantity (400–500 l. per minute) and at regular pressure. The funnel is connected below by a siphon-shaped elbow-pipe to a slightly inclined pipe also 250 mm. wide, while to the top of the conveyor is fitted a fume hood from which the acid fumes are drawn by the exhauster.

After being squeezed out the nitrated material is removed by means of tongs from the centrifugal to the conveyor, where it meets with a sufficient stream of water, which transports it through the conveyor pipes in any desired direction.

Generally each conveyor pipe discharges into a tank with perforated false bottom for the collection and preliminary washing of the nitrated material, otherwise the conveyor pipes from several apparatus may be all connected with one outflow pipe and discharge into a common receptacle.

The guncotton conveyor, in addition to being used for the hydraulic transportation of nitrated material wrung out of the acid centrifugal, may also be used for the transportation of material which has already undergone preliminary washing.

More recently[2], this firm has devized a guncotton washing

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[1] U. S. P. 638647, 1899; E. P. 11929, 1899; D. R. P. 107923; abst. J. S. C. I. 1899, **18**, 636; 1900, **19**, 492, 689; Chem. Centr. 1900, **71**, I, 1052; Wag. Jahr. 1900, **46**, I, 394.

[2] U. S. P. 1211450, 1917; abst. J. S. C. I. 1917, **36**, 238.

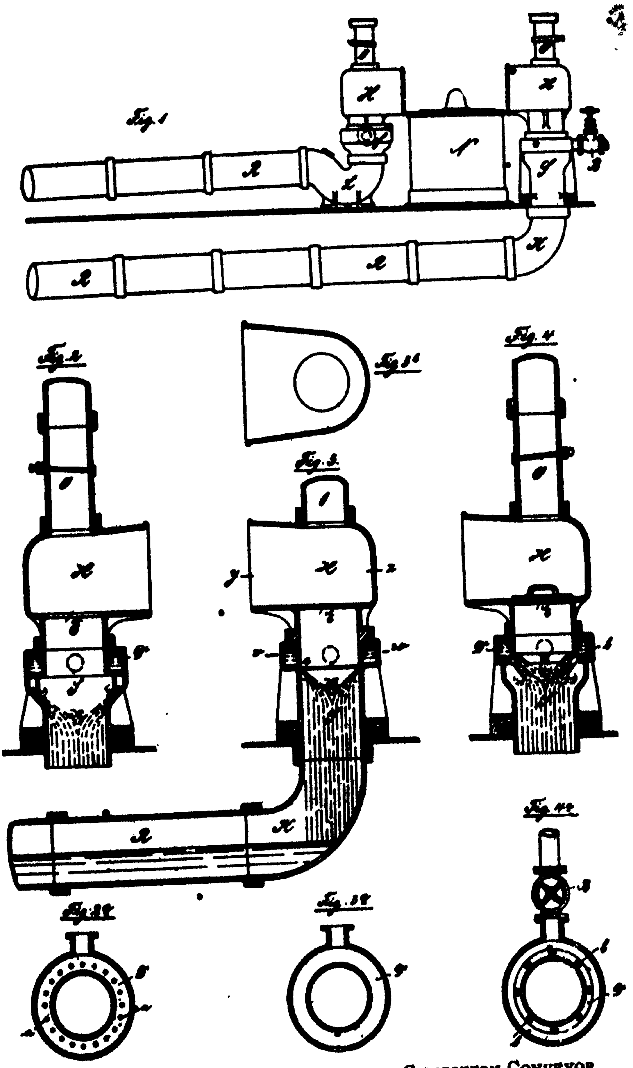

FIG. 209.—SELWIG AND LANGE HYDRAULIC GUNCOTTON CONVEYOR

apparatus in which the material is washed by passing it along a conveying tube into which, in two different places, water is supplied tangentially and obliquely downwards in the direction in which the guncotton is moving. Between the two water inlets is a chamber provided with a perforated wall forming part of the conveying tube; the wash water passes through the perforations to a drainage pipe outside.

At Waltham Abbey, England, it is understood this method of transportation has been tried, but with unfavorable results, although an apparently simple and practical method of transportation, presumably because it was found impossible or impracticable to bring the guncotton quickly enough into contact with a sufficiently large volume of cold water, the quality of the product often suffering as a result, and an unusually large amount of water being required for the method to operate efficiently.

Irrespective of the method employed, the object is to cool and dilute the nitrocellulose mass with its adhering nitric and sulfuric acids as quickly and efficiently as possible. From the nitrating apparatus after wringing or squeezing, the nitrocotton is dumped or transported to large wooden tanks filled with running cold water, preferably sand or sponge filtered, where the material is broken up by hand by means of long wooden paddles, a continuous stream of cold water being maintained by means of overflow plugs. After the nitrocotton has been so thoroughly washed in this manner that a piece withdrawn and squeezed in the hand tastes but faintly acid, the water is allowed to run off through a false bottom and wrung out in a centrifugal machine, or where possible, the last wash water is allowed to remain on the guncotton for several hours or better, over night, to extract the maximum of acid from the central canal of the cotton filament.

At this point the yield of the nitrating process is often conveniently determined by emptying the contents of a known number of pots or wringers in one vat, and after the preliminary washing as above followed by wringing, the entire product is placed in a tared truck and weighed, a representative sample being withdrawn for moisture determination. By this means it is possible to readily obtain the yield daily. In wringing nitrocellulose for determination of yield in the manner above indicated, it is useful to have a pipe with spray nozzle enter the wringer from the top, so that during the rotation of the machine a heavy stream of water constantly sprays on the nitrocotton packed against the periphery of the basket. In this manner the acid content of the nitrocellulose (expressed on the dry basis) can, by 20 minutes rotation, be reduced to less than 0.2%.

The apparatus of E. Loomis,[1] is adapted to mix nitrocellulose with water for the purpose of washing it, and conveying by a current of water. The material is suspended in a body of water, and passed out from the mixing apparatus through a tangential outlet.

F. du Pont has found[2] that when nitrocotton or similar substance is immersed in water which is in contact with air, and the whole agitated under pressure, causing solution of the air. The pressure is suddenly released causing the air to expand violently, dislodging impurities from the substance, and acting as nascent oxygen in oxidizing nitrous compounds to nitric compounds.

A variation of the method is to shower a mixture of water and nitrocellulose through compressed air, and to suddenly release the pressure from the mixture collected.

The Polytechnisches Notizblatt[3] recommend an "improvement" in the manufacture of guncotton, consisting in removing the acid only superficially, and then allowing it to lie "for a few days in the air" (perhaps? to ripen, mellow, mature or develop bouquet) before washing it free from acid. E. Schering[4] washes and bleaches at the same time by means of weak sulfurous acid in the wash water. It is stated that his celloidin for histological imbedding purposes is prepared in this manner.

J. Flack has developed an apparatus for drowning, washing and conveying nitrated cellulose shown in Figs. 210 and 211, which combines an elongated, shallow trough for the wash water, a stationary false bottom in the trough having its end spaced from the inlet and outlet ends of the trough, a device located

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1. U. S. P. 1324744, 1919; abst C. A. 1920, **14,** 468.

2. U. S. P. 648147, 1900, 724932, 1903; 762757, 1904; abst. J. A. C. S. 1903, **25R,** 520; J. S. C. I. 1903, **22,** 572; Mon. Sci. 1903, **59,** 163; Chem. Zts. 1904, **3,** 14. U. S. P. Re. 11651, 1898

3. Poly. Notiz. 1880, **35,** 287; abst. Wag. Jahr. 1880, **26,** 374; Chem. Ztg. 1880, **4,** 669; Chem. Tech. Rep. 1880, **19,** I, 340.

4. E. P. 4771, 1877; abst. J. A. C. S. 1879, **1,** 175; Chem. Ind. 1878, **1,** 368; abst. Ber. 1879, **12,** 310; Dingl. Poly. 1879, **231,** 94; Wag. Jahr. 1879, **25,** 420; Zts. Chem. Grossgewerbe, 1878, **3,** 860; Poly. Notizbl. 1879, **34,** 15; Chem. Tech. Rep. 1878, **17,** II, 166; Jahr. Chem. 1878, **31,** 368.

between for causing a movement of the water carrying the material towards the discharge end of the trough above the false bottom. After immersing and washing the nitrocellulose, the water is returned towards the inlet end below the false bottom, a screen being arranged at the discharge end to be a continuation of the false bottom for intercepting the cellulose material, yet permitting the water to pass, as well as a return passage for the water leading from the discharge end of the trough to the inlet end.[1]

The Flack apparatus seeks to reduce to a minimum the amount of water required, this being an adverse point in the use of this process of washing in general, the nitrated cellulose, however, being efficiently washed and simultaneously conveyed to the delivery point without undue waste of water.

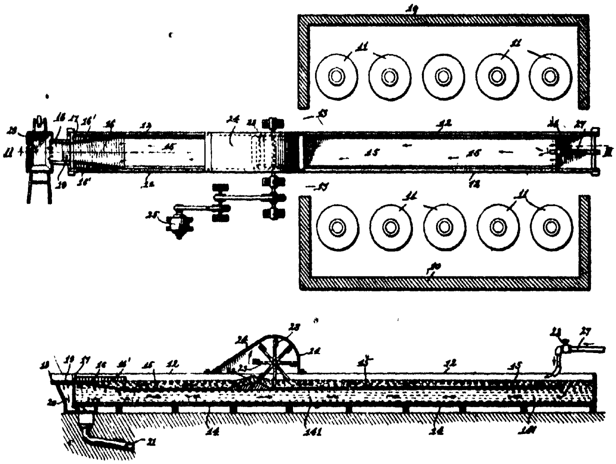

FIG. 210.—FLACK GUNCOTTON WASHER

Gebrüder Heine manufacture an apparatus for washing the nitrocotton and also filtering the waste waters from guncotton factories, comprizing a non-perforated drum with inner filter. The liquid to be filtered (containing solids in suspension) is placed in the non-perforated drum, the suspended material lodging against the side under the influence of centrifugal force, while the clear liquid is discharged through the central filter, through the core of the wringer. The clear liquid then runs through a suitable trough. When the circular section between the filter and walls of the drum is full of solid matter, it is cleaned out.

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[1] U. S. P. 1280981, 1918; Can. P. 183164, 1918; abst. C. A. 1918, **12**, 1348; 1919, **13**, 75; J. S. C. I. 1919, **38**, 29-A.

Selwig & Lange have constructed a guncotton floating apparatus[1] consisting in the main, of a stoneware funnel with widened lower part, connected with a stoneware pipe line of 250 mm. width, with a 2% fall. The pipe may also be advantageously constructed of aluminium. The water enters the upper part of the funnel at the rate of 350–450 liters per minute. The apparatus is covered with a hood by which the vapors are carried off with

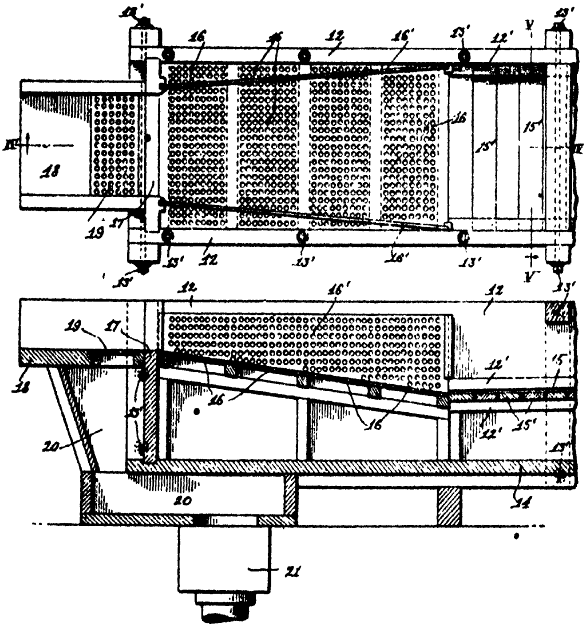

FIG. 211.—FLACK GUNCOTTON WASHER

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[1] D. R. P. 107923; abst. Chem. Centr. 1900, 71, I, 1052; Wag. Jahr. 1900, 46, I, 394.

the assistance of a fan. Several of the floating devices may be connected to the same pipe line.

G. Clark[1] in order to free pyroxylin from excess of acid, added an excess of sodium carbonate or bicarbonate to the wash water; while H. Anthony recommended ammonia for the same purpose,[2] but C. Weber[3] with others has found that the addition of ammonia to acid nitrocellulose is prone to explode, possibly induced by the inflammability of the ammonium nitrate formed thereon and therein. E. Hesketh and A. Marcet[4] render the wash water alkaline with soda ash, then tint it with litmus so that any acidity may be readily seen. The process would require *some* litmus for operation on a factory scale.

The apparatus of the Vereinigte Köln-Rottweiler Pulverfabriken[5] advize, instead of washing the nitrocellulose by displacing the nitrogen acids by water, to cause the nitrocotton to travel slowly through the layer of water. Risk of mixing the acids and water is thus minimized. The method of L. Van Schendel[6] is somewhat similar.

It has been stated that the higher the ratio of sulfuric acid to nitric acid in the nitrating bath, the more difficult it is to entirely free the nitrocellulose from acid, but there are other contributory factors which influence the difficulty of entire acid removal from nitrocotton. It appears that the lower nitrated cottons are more readily washed free from acid than those esters of higher nitration, but here again there are several modifying clauses necessary to this generalization, for it has been found that with low temperature of nitrating bath and high sulfuric acid content, the so-called "gelatinized" or "slimy" nitrocelluloses are formed which are very difficult to wash.

At the present time it is pretty well recognized that the addition of alkali, either volatile or non-volatile, is not good practice, and also that ultimate stability is best insured by conducting the earlier washing operations in an acid solution. With cold water washing, although considerable more time is required to arrive at a predetermined stability as compared with hot water washing, the color of the neutral nitrocellulose is appreciably lighter, and in some factories where hand nitration of paper is still carried on for the preparation of high class, water-white lacquers for the coating of silverware, cold water washing is still resorted to.

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[1] E. P. 3408, 1868; abst. Mon. Sci. 1870, **12,** 63; Deut. Industrieztg. 1870, 48; Wag. Jahr. 1870, **16,** 217.

[2] U. S. P. 143865, 1873; abst. Amer. Chemist; 1874, **4,** 279.

[3] J. S. C. I. 1893, **12,** 117, abst. Zts. ang. Chem. 1893, **6,** 405; Chem. Centr. 1893, **64,** I, 758; Jahr. Chem. 1893, **46,** 888; Chem. Ztg. 1893, **17,** 246, 1004; Chem. Ztg. Rep. 1893, **17,** 86; Chem. Tech. Rep. 1893, **32,** I, 238; Wag. Jahr. 1893, **39,** 428; Ber. 1893, **26,** 327-R; Meyer Jahr Chem. 1893, **3,** 249, 367; Industriebl. 1893, 158; Tech. Chem. Jahr. 1892-3, **15,** 171; Drug. Circ. 1893, 251; Proc. Amer. Pharm. Assoc. 1893, **41,** 441; 1894, **42,** 1200; Pharm. Ztg. 1893, 755. L. Paget, E. P. 7277, 1893; abst. J. S. C. I. 1893, **12,** 620.

[4] E. P. 3773, 1893.

[5] D. R. P. 307120, 1918; abst. J. S. C. I. 1920, **39,** 282-A.

[6] Belg. P. 200893, 1907.

Utilization of Wash Water. As far back as 1878 was realized the possibility of utilizing the water from washing the acid nitrated cellulose, for in that year V. Tribouillet and L. de Besauncele[1] obtained patent protection for a method of using the acid wash liquors from the manufacture of pyroxylin in making oxalic acid. It was also proposed to obtain dextrin in the same manner. The subject at the time, however, apparently excited but little attention, and it is only recently, that due to the issuance of several patented processes along this line, interest has again been aroused.

In the method as put forth by J. Umbach,[2] the nitrocellulose after centrifugalizing or pressing, is agitated with a solution of an alkali such as ammonia, and the mixed ammonium sulfate and nitrate washed out, evaporated to dryness, and either used direct as a fertilizer, or separated by fractional crystallization. According to the patentee, up to 95% of the acid remaining in the nitrocellulose can be thus recovered in the form of salts. According to C. Seyfferth,[3] successive charges of nitrocellulose are washed with the same wash water, which thus becomes gradually stronger in its nitric and sulfuric acids content, as the wash water is applied to material progressively stronger in adhering acid. The two acids are then recovered from the wash water in the customary manner.

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[1] E. P. 5057, 1878; abst. J. S. C. I. 1895, **14**, 180. See H. Eicheler, D. R. P. 323026, 1917.

[2] D. R. P. 309936, 1918; abst. J. S. C. I. 1919, **38**, 300-A, 806-A; Chem. Zentr. 1919, **90**, II, 126.

[3] U. S. P. 1248933, 1917; abst. C. A. 1918, **12**, 428; J. S. C. I. 1918, **37**, 75-A. E. Mann and J. Heess (E. P. 24938, 1913; abst. C. A. 1915, **9**, 1246; J. S. C. I. 1914, **33**, 859) have detailed the construction of a settling apparatus, applicable to the recovery of nitrocellulose.

The process of C. Claessen[1] is somewhat similar in that the wash water is used repeatedly to increase the concentration of acids contained therein, and is then treated for the recovery of the HNO_3 and H_2SO_4. For example, the nitric acid may be converted into nitric oxide by means of a reducing agent, such as ferrous sulfate, in presence of sulfuric acid, and the nitric oxide converted into nitric acid by the methods used in making nitric acid from atmospheric nitrogen.

W. Dreger has proposed an application of the principle of countercurrents to the washing of nitrocellulose. Six nitrating pans are placed in a circle, and a charge of cotton nitrated in each successively. Wash water is transferred from pan to pan in such a manner that each time it meets a more recently nitrated charge. By the time it has passed through five pans it has become moderately rich in acid, and in the sixth pan is used as the first wash of a freshly nitrated charge, after removal of the residual acids. It is then run off and collected.[2] Turigo has criticized—and justly—the above idea, drawing attention to the impracticability of the apparatus and method, non-uniformity of product, and greater cost of operation as compared with nitrating centrifugals.[3]

Closely allied to the subject of the utilization of the wash water, is the reclaiming of the nitrocotton present in the wash water. It is customary to pass the wash waters from the pulping, washing and finishing operations (but not from the acid boiling operation) through a series of settling tanks with baffle obstructions, to allow the suspended nitrocellulose to settle out. A proportion of this nitrocotton is so finely divided as to be almost if not quite in a state of colloidal solution or suspension, and passes away in the effluent. This effect is more noticeable when the water used is very soft, for in hard water the dissolved salts acting as electrolytes, appear to aid the deposition. The nitrocotton recovered in this manner invariably is found to possess a lower nitrogen content than the main product, and also usually has a lower stability. In plants which produce pyroxylin lacquers, artificial leather dopes and colored or opaque pyroxylin mixtures, this recovered nitrocellulose is kept separate and "worked in," usually in colored mixtures, preferably with pigments.

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[1] E. P. 6363, 1915; abst. C. A. 1916, **10**, 2800; J. S. C. I. 1916, **35**, 618. D. R. P. 288459, 1915; abst. C. A. 1916, **10**, 2300; J. S. C. I. 1916, **35**, 558; Chem. Zentr. 1915, **86**, II, 1092; Chem. Ztg. Rep. 1915, **39**, 466; Wag. Jahr. 1915, **61**, I, 278; Zts. ang. Chem. 1915, **28**, 632. Dan. P. 21341, 1916; Nor. P. 26996, 1916; abst. C. A. 1916, **10**, 2526, 3162.

[2] Zts. Schiess. Spreng. 1913, **8**, 325; Mon. Sci. 1915, **82**, 576; J. S. C. I. 1915, **34**, 576; C. A. 1913, **7**, 3840; Chem. Zentr. 1913, **84**, II, 1629; Meyer Jahr. Chem. 1913, **23**, 362; Wag. Jahr. 1913, **59**, I, 456.

[3] Zts. Schiess. Spreng. 1913, **8**, 397; abst. C. A. 1913, **7**, 4071.

Bleaching Nitrocellulose. The bleaching of nitrated cotton is seldom resorted to, but in nitrated paper intended for transparent celluloid sheets, and to a lesser degree nitropaper designed for the preparation of "water white" pyroxylin lacquers for application to white metal goods, are often given a light bleaching after nitration, and before the stabilizing washings have been made. Although bleached paper may be used as the form of cellulose to be nitrated, it has been found that a gentle bleach after the nitrating process is of value.

The three methods used in this connection are as follows:

1. Bleaching by chlorine (D. Spill process).
2. Bleaching by permanganate (J. Hyatt process).
3. Bleaching by oxalic and hydrochloric acids (invention of G. Mowbray).

In Spill's method the paper after nitration is given a slight wash to eliminate the bulk of nitrating acids, then placed in a cold solution of bleaching powder of 2° Twaddle strength (sp. gr. 1.01) where it is allowed to remain for from fifteen minutes to two hours with occasional stirring, and until a sample taken out and washed when held between the eye and strong daylight appears uniformly white and translucent. The excess of bleaching solution is then removed by a centrifuge, and the nitropaper washed in the usual manner until the desired stability tests are obtained. It has been stated that the use of warm or stronger bleaching-powder solutions is apt to result in the formation of chlorine substitution products, difficulty removable by poaching and washing, and which, when present, are prone to induce decomposition of the cellulose nitrate. The neutralized pyroxylin should show no traces of chlorides, when an acetone solution is mixed with a solution of silver acetate in ethyl alcohol.

The potassium permanganate method of bleaching has the advantage of being milder in action and more easily controlled. The paper fresh from the nitrating bath is several times washed to eliminate all but traces of free nitric acid, and plunged into a 1% solution of potassium permanganate, the pyroxylin taking on a light brown color from reduction of the permanganate. After agitating in the cold solution for a short time, steam heat is applied until a temperature of 40°–50° is reached, when dilute (10%) oil of vitriol is cautiously run in, still with continuous stirring, and until about 5% (calculated on the weight of the pyroxylin) has been added. After the acid has thoroughly permeated the contents of the tank, oxalic acid in aqueous solution is run in until the brown color of the pyroxylin just begins to lighten. By continued agitation the color gradually lightens until all the manganese dioxide has been oxidized, as shown by the appearance of a colorless solution again. If the solution does not become entirely colorless a second addition of oxalic acid is required. The nitrated paper is finally removed, washed free from acids and stabilized in the usual manner.[1]

In the process of G. Mowbray,[2] 25 lbs. oxalic acid and 15 lbs. HCl (strength not stated) are dissolved in 100 gal. water as nearly iron-free as possible. The oxalic acid is first dissolved and the HCl added cold. The nitrated paper in the proportion of 500 lbs. of pulp to 3 gal. of the above is placed in a hollander and there agitated until the nitropaper has assumed the pultaceous condition. Discoloration of the nitrocellulose from traces of iron is thus entirely obviated, the paper after being in contact with the oxalic acid mixture for several hours is then washed in cold running water until no test for oxalic acid can be obtained. Treatment in the usual manner follows.

In the dyeing of nitrocellulose, it is a point worthy of note, that the iron content of the nitropaper bleached after preliminary washing is considerably lower than when the bleaching operation has not been carried out. And furthermore, where this ferric stain is removed by bleaching, the brilliancy of the colors are enhanced, and their fastness often increased.

In determining the degree of bleaching of cellulose desirable, and the effect of the bleaching process on the nitrated cellulose, C. Piest[1] has found that the more strongly the cellulose has been bleached with calcium hypochlorite, the more washings will be required to affect the proper stabilization of the nitrated cellulose, and the greater will be the solubility of the final product in absolute alcohol.

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[1] To the washed nitrocellulose is added three times its volume of water containing 2% potassium permanganate, and then left for an hour in the cold. The unchanged permanganate is then washed out and a strong brine containing HCl is added. This mixture is allowed to act on the nitrocellulose until the latter has changed from a light brown or yellow to white, when all acid is removed by washing in the usual manner.

[2] U. S. P. 349658, 1886; abst. J. A. C. S. 1886, 8, 238.

It is claimed that paper or cotton bleached after nitration is more readily washed free from acids, more easily soluble in the usual solvents, and gives in addition to a more nearly colorless solution, one which will filter more readily and may be exposed to sunlight for a great length of time without assuming a yellowish tint. The use of sodium peroxide, hydrogen dioxide, or sodium perborate has not given as uniform or satisfactory results as the three methods described above.

Preliminary Boiling of the Nitrocellulose, usually spoken of as the "acid boil," is the first step in a series of operations for eliminating the extraneous acid on and in the nitrocotton, and to remove those bodies which diminish the stability, and introduced primarily as the result of the nitration process. It must be remembered that after nitration, the nitrocotton is in a most unstable condition due to the presence of adhering acid as well as acid remaining inside the cotton filament capillary, and in addition there is undoubtedly a large number of indefinitely characterized subsidiary products such as nitrated hydrocellulose, nitroxycellulose, nitrosugars, oxalic acid, oxypyruvic acid and other compounds contributory to instability. The sulfuric acid in combination as cellulose sulfonic or sulfonitric esters must also be removed before stabilization is satisfactorily completed.

Originally stabilization was effected by prolonged washing in cold running water, followed by a short treatment with an alkaline solution either cold, but more often boiling. Boiling, as now understood, did not form a part of guncotton manufacture in the earlier days.

The boiling is usually actually carried out in large circular wooden vats or tubs, about 9′ deep and 7′ internal diameter, with false wooden bottom about 6″ from the bottom, fitted with a steam coil containing a number of small perforations therein. No stirring arrangement is provided. The nitrocotton directly from the drowning tubs, after having undergone the preliminary acid wash, is either flowed to the preliminary boiling tubs, or more customarily is loaded on wooden trucks, and by means of a dummy railway pushed by hand to the boiling house. This is substantially a two-story affair, as shown in Figs. 212 and 213. The former illustration shows the boiling house of the du Pont plant at Old Hickory, and is typical of the present equipment in the United States. Fig. 213 illustrates the preliminary boiling house at the Ardeer factory of Nobel's Explosives Co., and shows the best arrangement in Great Britain.

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[1] Zts. ang. Chem. 1908, **21**, 2497; 1909, **22**, 1215; 1910, **23**, 1009; abst. Jahr. Chem. 1905–8, II, 973; 1909, **62**, 388; 1910, **63**, II, 423; C. A. 1909, **3**, 485, 2227; 1910, **4**, 2570; J. C. S. 1910, **98**, i, 464; J. S. C. I. 1909, **28**, 746; 1910, **29**, 841; Bull. Soc. Chim 1909, **6**, 232, 1165; 1910, **8**, 1563; Chem. Zentr. 1909, **80**, I, 474; II, 1090; 1910, **81**, II, 508; Meyer Jahr. Chem. 1909, **19**, 309; 1909, **19**, 335; 1910, **20**, 327; Wag. Jahr. 1908, **54**, II, 368; 1909, **55**, I, 431; 1910, **56**, I, 493.

The boiling vats have wooden tops with hinged covers (shown in the background in Fig. 213), the false or second floor being about 3′ below the top of the tubs. Each tub is provided with steam vent as shown. This operation is often spoken of as "percolator boiling," although, strictly speaking, it is not a boiling process as all, as the temperature in the tubs seldom exceeds 95°. There is a great variation in practice as to the number of "boils" and the duration of each to which it is advizable to submit the nitrocotton. Bruley[1] has shown that prolonged boiling increases the solubility and lowers the percentage of nitrogen in the guncotton. C. Haeussermann[2] has reported the formation of an oxime compound of an aldehyde or ketone on boiling nitrocellulose with alkali. Then there is the question as to whether *actually* boiling with steam to eliminate acid does or does not hydrolyze the nitrocellulose. Certain it is that some change occurs which is not apparent when water at not to exceed 95° is used, and this change is shown by the nitrated cotton

[1] Mem. Poudres. 1895–6, **8**, 131; abst. Meyer Jahr. Chem. 1897, **7**, 301. Practical experiments in the washing of centrifugally esterified cellulose of the kind used for pyrocollodion smokeless powder, and with the usual drowning operation and cold water wash, have shown that the free nitric and sulfuric acids present are entirely removed so far as acidity tests go, by seven hot water washings of three hours each, where the decantation is 60%, i. e., where 60% of the bulk of water originally present was discarded by draining.

[2] Ber. 1903, **36**, 3956; 1904, **37**, 1624; abst. Wag. Jahr. 1903, **49**, 345; 1904, **50**, 357; 1908, **54**, I, 357; Meyer Jahr. Chem. 1904, **14**, 370; Jahr. Chem. 1903, **63**, 1017; 1904, **57**, 1168; Chem. Centr. 1904, **75**, I, 160, 1405; J. S. C. I. 1904, **23**, 36.

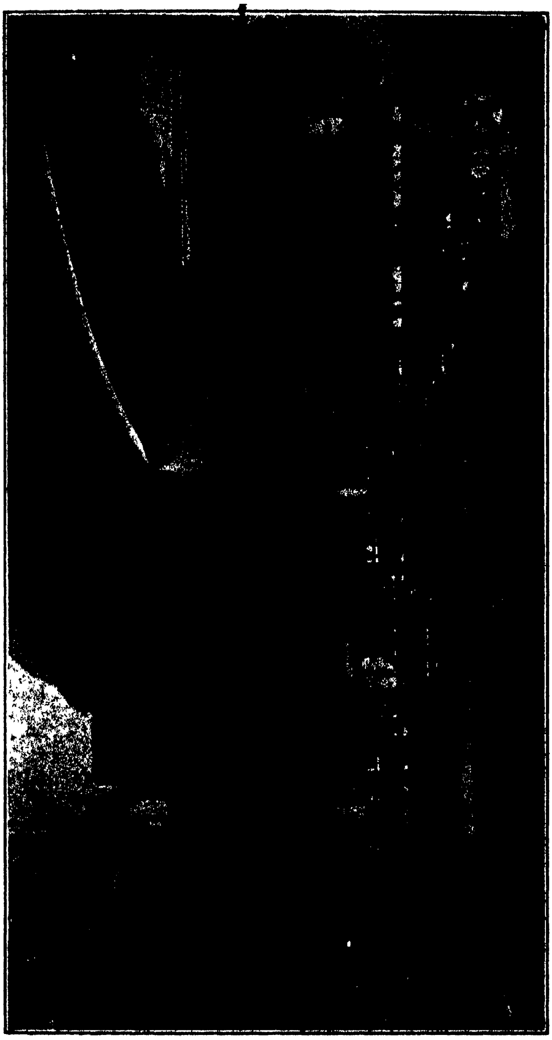

Fig. 212.—Percolator Boiling Tub House (E. I. du Pont de Nemours Co.)

giving a cloudy solution with various solvent mixtures, in which it otherwise would dissolve clear. Furthermore, the temperature of boiling is intimately associated with the precipitation of flocks or granules upon standing, in a nitrocellulose solution which has been once clarified by paper filtration. Those pyroxylins which have been boiled by live steam appear to be much more prone to "granulate" in solution upon long standing. This is a very important point in the pyroxylin lacquer industry and the artificial filament and photographic film arts.

There is no doubt but what one of the most important functions of the preliminary boiling operation is to remove the sulfuric acid in combination, and this is more speedily and efficiently brought about by conducting the operation in a slightly acid medium. A large manufacturer of pyroxylin for photographic use in the United States does not pulp the nitrocotton on account of the fact that this process introduces a small amount of iron (from 0.01% to 0.03% calculated as Fe_2O_3) and makes a considerable observable difference in the color of the solution from which the films are cast. Instead a series—usually 12—washes of 10 hours each in water between 80° and 90° are given, the nitrocotton being allowed to stand in water over night between the "boils," and protected from the light and dust by means of canvas coverings.

Boiling for five periods of ten hours each, requiring five days time, has in general been found quite satisfactory, but the methods and directions for the length of time of an individual "boil" and the number required, vary greatly. A cycle constituting a "boil," is considered the length of time of a complete cycle of filling the tub with water, the actual heating operation, allowing the hot water to run out, the draining, and up to the point of re-filling the tub. With a ten hour boil per day, the nitrocotton is allowed to soak in the hot water at the close of the ten-hour heating period until the next day, and this has been found efficient, especially from the view point of minimum water consumption. Irrespective of the special number or rotation of the series of these washings, at the conclusion of the last boil, the nitrocotton is substantially neutral, and the last wash water should not more than faintly redden neutral azolitmin solution.

It is customary to make a stability test upon the nitrocotton

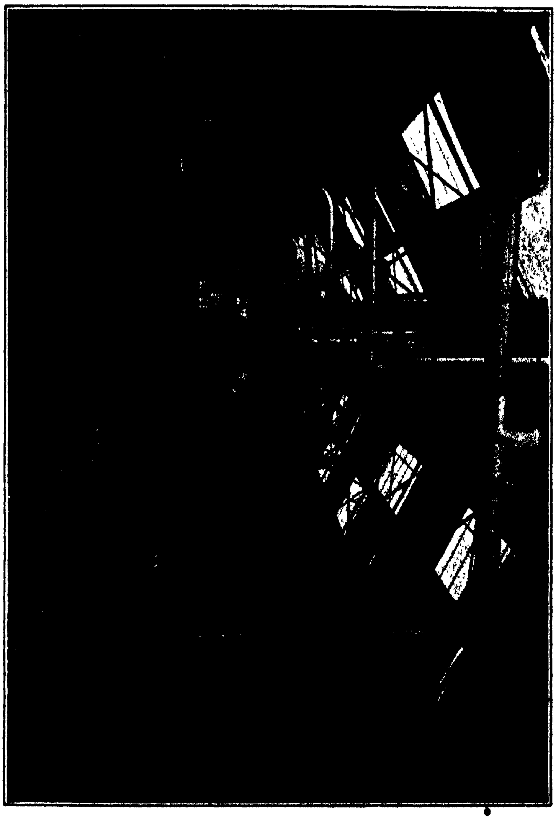

Fig. 213.—Guncotton Boiling House (Nobel's Explosives Co. Ardeer Factory)

at the close of the last preliminary boil in order to approximate the degree of stabilization which the material has undergone as the result of the processes to which it has been subjected up to this point.

Many methods have been proposed from time to time to most economically and expeditiously effect this preliminary purification, some of which apparently are devoid of merit, or else so cumbersome, time consuming or expensive as to be precluded in commercial manufacture. In 1872, S. Mackie[1] designed a "guncotton engine" for the washing of nitrated cotton, and subsequently amplified and improved upon.[2] J. Hyatt and J. Jarvis in 1878[3] devized an improvement in apparatus for washing paper pulp, especially applicable to the celluloid industry. G. Clark[4] had previously experimented along similar lines.

According to F. Nathan,[5] in England, in the official "Notes on Gunpowder and Guncotton," published by the War Office in 1878, it is stated that guncotton manufactured at Waltham Abbey underwent two boilings by steam in wooden vats for 8 hours each, the water being extracted after each boiling by wringing for 3 minutes in clean water centrifugal machines. The same boiling process was in use in 1888, according to a later edition of the same book. Five years later each boiling was extended to 12 hours, and the boiling lasted for 5 days and nights—that is, the guncotton received 10 boilings of 12 hours each. In April, 1894, this system of boiling was replaced by a system characterized by short boilings at the commencement of the process, the time of successive boilings being gradually increased. The scheme of boiling was as follows:

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[1] E. P. 2693, 1872; abst. Ber. 1874, **7**, 741; Poly. Centr. 1874, **40**, 789; Dingl. Poly. J. 1874, **213**, 74; Bayr. Ind. u. Gewerbebl. 1874, 276; Chem. Tech. Mitth. 1874–5, 218.

[2] E. P. 13903, 1890. See also E. P. 5917, 1890.

[3] U. S. P. 210612, 1878.

[4] Mon. Sci. 1870, **12**, 63; Deut. Ind. Ztg. 1870, 48; Wag. Jahr. 1870, **16**, 217. J. S. C. I. 1909, **28**, 177, 181; abst. C. A. 1909, **3**, 1342; Chem. News, 1909, **99**, 83; Bull. Soc. Chim. 1910, **8**, 60; Mon. Sci. 1910, **72**, 111; Rep. Chim. 1909, **9**, 376; Chem. Zentr. 1909, **80**, I, 1678; Chem. Ztg. 1909, **33**, 208; Chem. Ztg. Rep. 1909, **33**, 146; Jahr. Chem. 1909, **62**, II, 388; Meyer Jahr. Chem. 1909, **19**, 333; Wag. Jahr. 1909, **55**, I, 431; Zts. ang. Chem. 1909, **22**, 1614; Zts. Schiess. Spreng. 1909, **4**, 285, 327.

[5] J. S. C. I. 1909, **28**, 177; abst. C. A. 1909, **3**, 1342; Jahr. Chem. 1909, **62**, I, 388.

No. of Boiling	Duration in Hours	No. of Boiling	Duration in Hours
1	2	7	6
2	2	8	6
3	4	9	9
4	4	10	9
5	6	11	12
6	6	12	12

This system of boiling was continued with but slight modifications until August, 1905. On the introduction of the displacement dipping process it was found, as already stated, that guncotton made in this way was brought to a condition of stability by the boiling process then in use, and just referred to, at an earlier stage, than guncotton made by the Abel process. A probable explanation of this fact is that during the displacement process a zone of acid liquid at a comparatively high temperature—somewhere about 40° C.—passes through the whole of the guncotton in the dipping pan. The action of this hot acid liquid may be to oxidize certain organic impurities which are certainly present, and to cause the breaking-down of unstable nitrogen compounds into soluble or non-reactive bodies. Systematic experiments were therefore carried out, in 1905, to determine the most suitable and most economical method of purification by boiling, for displacement process guncotton. In the principal experiments two types of boiling were employed—one in which long boilings were used at first, followed by short boilings; the other in which short boilings were used at first, followed by long boilings. The following deductions were made from the results obtained in these experiments:

1. Purification of guncotton obtained by means of long boilings at the beginning followed by shorter boilings later, is superior to that obtained when the reverse condition holds. This is substantiated by the following considerations: Examination of the waters showed that neutrality is obtained earlier; that less decomposition of the guncotton takes place; that the stability, as shown by the various stability tests, is greater; and that a stable condition is attained earlier.

2. A displacement washing after a long acid boiling at an

early stage is a beneficial treatment. This treatment is probably responsible for the early attainment of neutrality.

The system of boiling determined on as a result of these experiments was as follows,

No. of Boiling	Duration in Hours	No. of Boiling	Duration in Hours
1	12	6	4
2	12	7	4
3	4	8	2
4	4	9	2
5	4	10	2

with a cold water displacement wash after the first two boilings.

Several processes have been brought forward for the stabilization of nitrocotton by boiling under pressure, in which apparently are embodied points of merit. In the method of the Vereinigte Köln-Rottweiler Pulverfabriken,[1] the nitrocellulose was both stabilized and disintegrated by a few hours boiling under pressure, it having been found that by increasing the pressure sufficiently the material is reduced to the state of a fine powder. According to the authors' experience, boiling a nitrocellulose under a pressure sufficient to insure its disintegration, hydrolyzes the ester so that the viscosity is materially reduced, and the solubility affected correspondingly.

F. du Pont immerses the nitrocellulose in water which is in contact with air, and the whole agitated under pressure, thus causing the solution of the air. The pressure is then suddenly released, thus causing the air to expand quickly, the effect being, according to the claims of the patentee, to cause the air which has penetrated the interstices of the cotton fiber, or perhaps the inner filamentous canal, to suddenly inflate, dislodge impurities, and cause the nascent oxygen to oxidize nitrous to nitric acid compounds. A variation of the method is to shower a mixture of water and nitrocellulose through compressed air, and to suddenly release the pressure from the combined mixture. The idea appears to the author to be decidedly ingeneous—and that is all.[1]

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[1] E. P. 5830, 1900; abst. J. S. C. I. 1900, **19**, 403, 492, 560; Mon. Sci. 1902, **58**, 166; Chem. Ztg. Rep. 1901, **25**, 648; Chem. Tech. Rep. 1901, **40**, 572. F. P. 398672, 1900; abst. Mon. Sci. 1901, **57**, 304. Belg. P. 148850, 1900.

The Société anonyme de produits chimiques de Droogenbosch[2] stabilizes after washing and drying the nitrocellulose, a product designed to be especially applicable in the artificial silk industry. In proceeding according to the directions as laid down by the patentees, the nitrocellulose is washed in the usual manner until apparently free from acid, then carefully dried by being placed in thin layers on tinned copper or copper wire screens. A portion of the air used to drive off the moisture, before its entrance into the nitrocotton dry chamber, passes through a closed box, on the bottom of which is spread an intimate mixture of slightly hydrated quick lime and ammonium carbonate. The effect of the lime upon the ammonium salt, is the liberation of ammonia, which is then slowly aspirated over the surface of the damp nitrocellulose.

The National Explosives Co. and W. Bate,[3] wash nitrated cotton by the continuous (as distinguished from the usual intermittent) introduction of hot or cold *distilled* water into the washing vessel so as to displace the acid liquid upwards or downwards, the water being supplied at such a rate and in such a volume that displacement takes place practically without mixing.

In 1903 Selwig and Lange[4] introduced a method whereby the nitrocellulose or similar nitrated substances are steamed and washed in a centrifugal, which method has decided points of merit. Their apparatus, called a "guncotton steam centrifugal," and shown in Fig. 214, consists of a closed cylindrical vessel with inclined bottom, in which a centrifugal basket is so fitted that it may be rotated. The vessel is provided with a tightly fitting lid, on which are arrangements for admitting steam, or steam and

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1. U. S. P. 724932, 1903; 762757, 1904; abst. J. A. C. S. 1903, **25R,** 520; 1905, **27R,** 60; Mon. Sci. 1903, **59,** 163; 1905, **62,** 15; Chem. Zts. 1904, **3,** 14.

2. E. P. 5076, 1901; abst. J. S. C. I. 1902, **21,** 546; Mon. Sci. 1905, **62,** 322. Belg. P. 155185, 1901.

3. E. P. 128978, 1917; abst. C. A. 1919, **13,** 3013; J. S. C. I. 1919, **38,** 698-A.

4. E. P. 6409, 1903; abst. Arms and Explos. 1304, **12,** 54; J. S. C. I. 1904, **23,** 337. F. P. 327803, 1902; abst. J. S. C. I. 1903, **22,** 963; Mon. Sci. 1904, **62,** 47; 1905, **63,** 83. D. R. P. 150319; abst. Mon. Sci. 1905, **63,** 14, 322; Chem. Centr. 1904, **75,** I, 1187; Chem. Ztg. Rep. 1904, **28,** 411; Chem. Zts. 1905, **4,** 197; Jahr. Chem. 1904, **57,** 1168; Wag. Jahr. 1904, **50,** I, 346. Swiss P. 27809, 1903. Belg. P. 169185, 1903.

air to the interior of the basket, or also to the outside. Cold or hot water, as desired, may be admitted to the interior.

The steaming process is conducted as follows: Wet guncotton, either fibrous or pulped, is filled into the centrifugal drum which is then set in motion, and after the cover has been closed, dry, high pressure steam which may be mixed with air to moderate the temperature is admitted. The steam penetrates the nitrocotton which is pressed against the sides of the basket, heats it uniformly, and thereby destroys the unstable products contained therein. These are dissolved or emulsified in/by the condensed water, and are immediately removed by the centrifugal action. At the close of the steaming process, the guncotton is left in the still revolving basket, and washed first with hot and

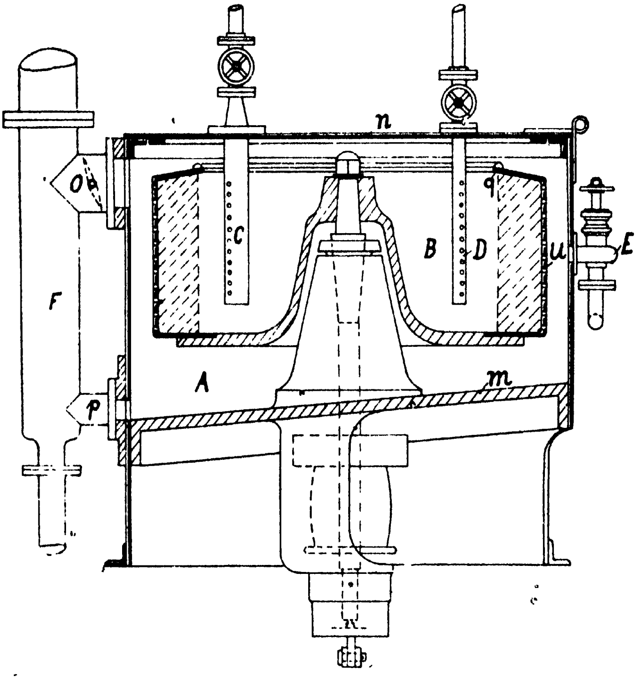

FIG. 214.—SELWIG & LANGE GUNCOTTON STEAM CENTRIFUGAL

then with cold water, being finally wrung until all the water has been expelled that is removable at the speed of the centrifuge. The steaming process may also be alternated with washing.

In washing nitrocellulose, to remove resinous and other impurities contained therein, J. Duclaux[1] recommends treatment with benzene, toluene, xylene, carbon tetrachloride, chloroform or similar haloid substituted aliphatic hydrocarbons, followed by treatment with hot water until all the volatile solvent has been eliminated.

In this process of stabilization, as carried out in several factories in Great Britain, where the boiling is conducted in large vats accommodating 1,000 to 2,000 lbs. of nitrocotton, instead of heating with steam by perforated coils *below* the perforated wooden false bottoms, the steam is also supplied through central puffer pipes on the principle of a vomiting kier (see p. 596), in which case, the heating of the mass in the kier is from tne top downwards. In tnis arrangement, as where the heating is from the bottom upwards, wooden vents or chimneys are fitted to the lids of the vats to carry off the spent steam, as shown in the accompanying illustrations. For certain special purposes, where the absolute exclusion of woody particles is necessary, and the color of the nitrocotton is of great moment, the vats may be lined with earthenware tile or sheet lead. Other linings, such as sheet iron covered with lead by the Cowper Coles process, and bakelite, both as a paste and by impregnation, have been tried but without success In isolated instances, reinforced concrete vats have been used, but soon cracked, due to the strain of alternate heating and cooling.

As to the nature of the boiling, no hard or fast rules, or uniform method of practice can be laid down which will be generally applicable, the treatment required depending on a number of factors, including the character of the nitrocotton, method of nitration, ratio of nitric to sulfuric acids in the nitrating bath, degree of nitration, nature of the water supply available, and the special purpose to which the nitrocotton is to be put.

When made by the displacement process for example, the product may be stabilized by about 30 hours boiling, whereas

[1] E. P. 130619, 1919; abst. J. S. C. I. 1919, **38**, 610-A; 1920, **39**, 388-A. F. P. 461785, 1914; abst. Mon. Sci. 1914, **81**, 122; Chem. Ztg. Rep. 1914, **38**, 349.

by another method of nitration, 80 to 90 hours boiling may be necessary. On the other hand, nitrocelluloses of low nitration for special purposes, as for example, blasting explosives, are in the main more easily stabilized, and are merely treated with hot water, due to the lowering effect on the viscosity which boiling induces. In general—but not always—the higher the degree of nitration, the more drastic and prolonged will be the stabilization required. Nitrocotton intended for water-white pyroxylin lacquers receives a very mild stabilization treatment in order to conserve the color and preserve the viscosity. The method of stabilization of J. Stevens,[1] consisting in washing with water and then subjecting the nitrocellulose to an aqueous solution of urea as an ant-acid, is more applicable to pyroxylin plastics. It has been noted that those nitrating mixtures relatively high in sulfuric acid, produce nitrocelluloses more difficult of stabilization, but the reason is not on account of a higher percentage of conjugate sulfates present in the nitrocellulose—at least not entirely so.

The general principles of practical stabilization (for the *theory* of the subject, see p. 1700) are primarily based on the fact that in addition to adhering acids on and in the cotton filaments, the nitrocotton contains small amounts of sulfuric or mixed nitrosulfuric esters and other unstable bodies which must be broken up and eliminated to avoid the development of free acid, and consequent instability when the nitrocotton is stored.

As has been mentioned, free sulfuric acid is especially objectionable and a prime factor in incipient decomposition of all cellulose esters, as it is non-volatile and remains unchanged, in which condition it undoubtedly acts as an autocatalyzer in promoting decomposition. It has been pretty well established that an initial acidic treatment is the proper method to pursue for the hydrolysis of these esters, and should usually be followed by treatment in a mild manner with weak non-volatile alkaline solutions to complete the stabilization. Alkaline treatment however, also readily hydrolyzes nitric esters, and should therefore, be prolonged no longer than necessary. Unduly prolonged boiling has been found to exert a lowering effect on the stability.

Irrespective of the method followed on the manufacturing scale, the progress of stabilization should be followed by progressive heating of the nitrocellulose with water, and examination of the various wash waters for reaction, sulfates, nitrates, nitrites and other oxidizable bodies, as well as the elimination of the free nitrating acids, and the hydrolysis of the esters.

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[1] U. S. P. 605931, 1898; abst. Mon. Sci. 1898, **51**, 266; Chem. Ztg Rep. 1898, **22**, 565.

The rate of elimination is found to progressively decrease, and after a time to reach a constant which may be safely taken as indicating that the impurities have been sufficiently removed, and that the nitrocotton only is being decomposed. The residue upon evaporation of the wash waters, especially in the earlier stages of the boiling, yields a somewhat complex mass which can be separated by treatment with suitable solvents and reagents into a large number of bodies of distinctive character, some of which are crystalline, but the majority being amorphous. Some are so unstable as to explode if drying is attempted.

While the wash water tests are only indicative, they are valuable indications as showing the progress of stabilization, and must be supplemented by a testing of the nitrocotton itself at the various stages, as outlined in the succeeding chapter, and of these tests, those which show the degree of resistance of the explosive to decomposition when exposed to more or less intensified conditions, must however, be mainly relied upon. These tests, as will be explained further on, are primarily based on the qualitative detection or quantitative measurement of the nitrogen oxides evolved when the nitric ester is heated.

Pulping the Nitrocellulose, also frequently referred to as "beating," for the reason that the fibrous material is *beaten* to a *pulp* by frictional blades, is a process, which was suggested by J. Tonkin (see p. 1604) but developed along the practical lines of the treatment of guncotton by F. Abel, and from his investigations, has come down to the present time with many minor improvements in efficiency and output per unit of time.

The guncotton produced in the earlier days of the art was, as has been pointed out, purified mainly by simply washing in cold water, the washing sometimes being prolonged for several weeks time, and it is primarily due to this inadequate treatment that the numerous explosion of those times must be attributed. One of the improvements of v. Lenk (see p. 1593) was the introduction of boiling for 15 minutes with a weak potassium hydroxide solution, but at that time the idea seemed to prevail that it was only necessary to eliminate the free acid in the nitrocellulose, in order to obtain a perfect stability. The presence of other nitrated bodies and sulfuric acid combinations apparently were not suspected, and certain it is, that their effect on producing instability was insufficiently recognized, and the necessity for their elimination only superficially appreciated. Furthermore, it has been demonstrated that the unpulped nitrocotton retains acid in the capillary tubes with almost incredible tenacity. For instance, if the nitrocellulose is washed in water until apparently all the acid has been removed as shown by delicate indicators, and the fibers are then pulped subsequently, the water in which the comminution has taken place will show a decided acid reaction. A most thorough comminution of the fibers is therefore necessary, in order to open them up, and lixiviate them. Nobel's Explosives Co. have found by direct microscopical examination, that one gram of normally pulped guncotton may contain as many as seven million distinct fibers.

Since pulping was introduced in England about 1865, it has formed an essential part of the treatment of nitrocotton intended for explosive purposes, as distinguished from the peaceful arts, where for obvious reasons, the stability of explosives, has, until recently, not received the attention which the importance of the subject merits. By reducing the fibers to a fine state of subdivision, it not only brings the nitrocotton into a much more compact condition, but greatly facilitates washing and blending. The method of E. Nicholson[1] of adding litmus, blue archil or similar indicator so that any acid developed by subsequent spontaneous decomposition can be discovered in time, is not employed at the present time, if ever.

The operation is carried out in pulping or beating machines similar to those used in paper making. Typical of this practice is the hollander pulper as used by Nobel's Explosives Co. and illustrated in Fig. 215, and in the United States by the Miller Duplex Beater, as indicated in Figs. 216 and 217. In the former illustration, the method shown is carried out as follows: The pulping machine consists of a trough or casing, which may be of iron or ferro-concrete, in which a revolving power-driven roller armed

[1] E. P. 2430, 1871; abst. Bull. Soc. Chim. 1872, **17**, 479.

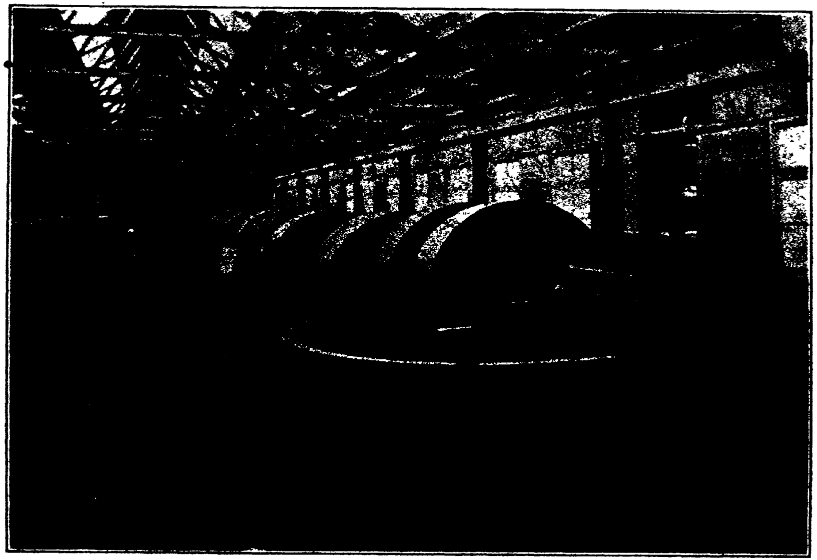

Fig. 215.—Installation of Hollander Pulper Showing Roller Blades (Nobel's Explosives Co.)

with steel blades, operated against a block or bed plate of blades fixed in the casing. The nitrocotton is suspended in about ten times its weight of water, and by the action of the roller, which also acts as a paddle, is made to circulate and pass re-

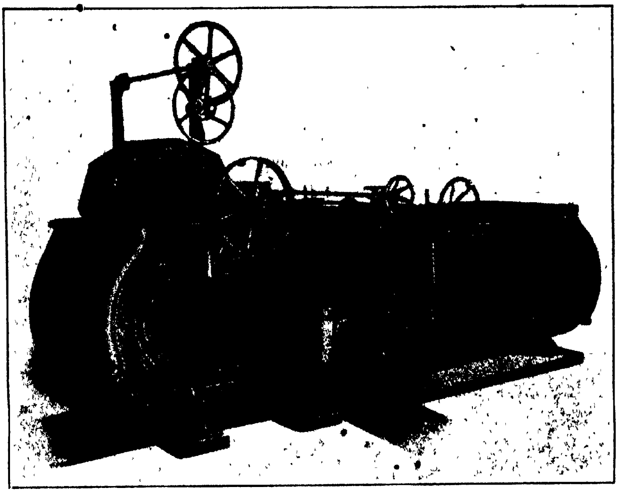

FIG. 216.—THE MILLER PATENT DUPLEX BEATING ENGINE

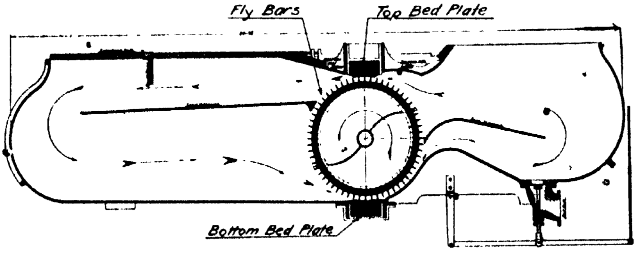

FIG. 217.—MILLER DUPLEX BEATER

peatedly between the two sets of blades until reduced to the state of fineness required. The blades in the roller are placed parallel to the roller axis, whereas those in the block are fixed at an angle, the cutting power being in this way increased. Of the various types of these machines, some circulate the pulp horizontally, and in others the circulation is in a vertical direction. The hollander (shown in Fig. 215), introduced in Holland for paper making about 1750, may be taken as representing the former type, and the Umpherson and Hoyt the latter.

The period of pulping varies with the size and type of the pulper, and the purpose for which the nitrocotton is to be used, but from two to four hours is generally found sufficient. In certain special cases, and with hard fiber nitrocottons, longer pulping up to 6 hours may be required. In general, the lower the nitration (percentage of nitrogen in the nitrocotton), the shorter is the time of pulping necessary, this being a generalization which does not always hold true. The fineness is judged by the feeling, and by the appearance of the fracture when a handful is squeezed to remove excess of water and broken across. A settling test in which a weighed quantity of the dry nitrocotton is shaken up in a cylinder with water, and the apparent volume of the pulp noted after settling, is used as a control. For the measurement of the actual length of the fibers, microscopic examination, of course, is necessary.

In the pulping of cellulose for paper making, a crushing or grinding action is mainly required so that the fibers may be left in a torn and ragged condition with increased felting properties. Of importance also to the paper maker is the hydration or gelatinization of the cellulose which occurs in pulping, for this assists in the agglutination. These effects are promoted by the use of somewhat blunt blades, necessitating more or less prolonged treatment. With nitrocellulose on the other hand, what is most desired is a sharp cutting action in order to reduce the material as quickly as possible before hydrolysis sets in. Sharp blades are therefore desirable. With blunt edges there is a tendency for clusters or aggregations of fibers to be formed, which appear flattened, as on an anvil. This flattening effect is readily observed by making a dilution test, and observing the broken filaments microscopically.

During pulping a certain proportion of iron in a finely divided condition is ground off the blades, and as this may induce chemical action on the nitrocellulose during storage, bronze blades have been tried to prevent its formation, but this has been found to result in a much lower output. Electromagnets, as described later, are therefore used for the elimination of this iron.

In the United States, the beater which has probably been most extensively used for the comminution of all forms of nitrocellulose is the Miller Duplex Beater as manufactured by the Downingtown Manufacturing Co., East Downingtown, Penna. In addition to the general illustration of this machine as shown in Fig. 216, is the section in Fig. 217.

The sides, bottom and midfeathers are of cast iron, with covers of 3" cypress securely bolted to the tub sides, and provided with openings for furnishing and washing, or the top may be left entirely open. The fly bars are all steel, laid steel or bronze, the apparatus being equipped with two beaters, one under the roll and one on top. This greatly adds to the efficiency of the machine by cutting down the time of pulping to any desired degree of fineness. The roll and the top plates are adjusted by the one handwheel which raises and lowers the lighter bars, by which the top plate is raised two units for each single unit which the roll is raised. In other words, the top plate is actuated in both directions twice as far as the roll. This keeps the spacing between the roll and the two plates the same in any and all positions of the roll. The location of the roll in the center of the tub, submerged between the two bed plates and horizontally between the front and rear midfeathers, divides the tub into two horizontal planes, under and above which the stock is rapidly circulated.

The stock travels many times faster in this type of beater than in the old fashioned hollander, and is subjected to two beating operations each time it completes an entire circle around the tub. It, therefore, performs its work in much less time than that consumed in the holland type of engine, and also does the work more thoroughly and efficiently, as there is little chance for the material settling in any part of the tub. In the reduction of nitrated cotton this type of beater is especially applicable, as this material has a great tendency to settle as soon as the fibers become shortened by cutting, requiring hand stirring and paddling to prevent settling, and consequently uneven reductions.

With a machine of the above type, no stirring is required, the engine being adapted to the beating of all forms of nitrocellulose. The largest power consumed by any beater, is the power required to circulate the stock. The most efficient beater, therefore, increases the beating effect in proportion to the circulation. The above Duplex beater is the only type to the author's knowledge which effects two beating operations for every circulation of the stock through the tub. About 60 h. p. is necessary to properly run this beater under full load. If the beater is to be electric driven, a 75 h. p. direct current motor is better. With an A. C. motor, the speed drops off as the load increases, which is exactly what ought not to happen in the case of a beating engine, since it is necessary to keep up the speed in order to secure proper circulation of the nitrocotton. If a D. C. motor is installed, a constant speed may be maintained with comparatively little variation, regardless of the load.

The best speed of this beater is 120–130 r. p. m. By changing the speed from 112 r. p. m. (that recommended by the manufacturers) to 130 r. p. m., a charge can be pulped in 8 hours, whereas with the lower revolution, 10–12 hours is usually required. A normal charge is 1500 lbs. nitrocotton per beater, and under favorable conditions, three beaters may be run off per 24-hour day.

The claims put forward by the manufacturers of this machine are as follows:

1. The length of fiber can be reduced to as fine a condition as required in the minimum of time, due to the double beating operation.
2. The charge when reduced is found to be very uniform.
3. The fly bars may be removed and inserted without dismantling, and with ordinary mechanical labor.
4. The emptying and washout valves are operated by levers from above the working floor.
5. The beater roll is "bandless." The fly bars are made so that the section in the head is a fit in the dovetail slots.[1]

At Picatinny Arsenal, Dover, N. J., where these beaters are used, hot, and not cold water is run in, this being made possible by the installation of an iron tank about 3′ diameter and 10′ high, enclosed, through which waste steam is passed, and from this, the heated water is run into an elevated wooden tank, of capacity sufficient to feed three beaters. Considerable saving in time in beating is effected by proceeding in this manner.[1]

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[1] In setting up the pulper the bottom bed plate should be set perfectly level, and the roll so adjusted that it will touch the bottom plate evenly from end to end, the top plate then being screwed down until it also touches the roll bars evenly. This adjustment should not again be touched until the wear on the rolls makes a new adjustment necessary. Adjustment while running is made from the main handwheel on the lighter bars of the roll. The combined leverage of the roll lighter and the short lighter operating the top plates is so proportioned that when the roll is raised one unit the top plate is raised two units, thus making the space between the roll and top and bottom plates always exactly the same. Care should be taken not to tighten

The efficiency—amount of nitrocellulose which a beater will properly pulp in a given time—varies greatly with the type of nitrocellulose, to which attention has been previously drawn. With a comparatively soft nitrocellulose, e. g., with a low nitration and high solubility in ether-alcohol, as the pyroxylins and collodion cottons, much more can be pulped in a given time than with the highly nitrated and tougher nitrocottons, insoluble in alcohol-ether, and 12.9%-13.2% nitrogen. With the latter, a much longer time is usually required to comminute them to the required degree of fineness.

Excessive pulping affects the solubility. It is a curious fact, not generally known, but one which the author has repeatedly verified, and that is that the addition of a minute amount of a nitrocellulose solvent as (0.1% acetone) to the water in the beater, will materially decrease the time of beating. Whether the small amount of solvent added is sufficient to intumesce or soften the nitrocotton, is a question.

There is no doubt that the very long staple guncotton before pulping retains in its tubes unstable bodies which no reasonable amount of boiling will remove. The effect of pulping being to materially reduce the length of the individual filaments, it must at the same time produce a certain amount of crushing in them. This allows of impurities being removed, both mechanically as by attrition, and by diffusion, solution, emulsification or saponification.

The mechanical efficiency of a pulper depends upon a number of factors, including the shape of the trough, the number and length of the blades in the roller and block, the angle of inclina-

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up the top plate box too much, sufficient to prevent vibration being all that is necessary, as otherwise there might be difficulty in raising or lowering the plates. A spring is provided, the function of which is to admit of adjustment of the top plate; the manufacturers recommending that this spring be maintained at its maximum compression.

[1] H. Schulte, Zentr. Oestr-Ung. Paperind. 1914, **28**, 871; abst. Paper, 1915, **15**, No. 24, 15; C. A. 1915, **9**, 1114.

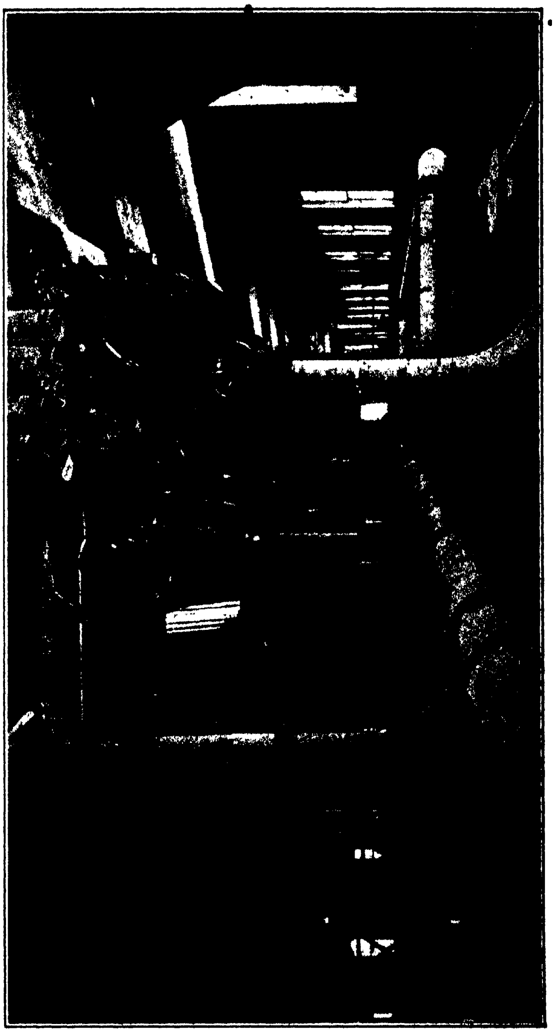

FIG. 218.—PULPING HOUSE, SHOWING CORLISS ENGINES

tion of the blades, the circumferential speed of the roller, and especially is it of importance that adequate power be provided so that the maximum of cutting force may be exerted. The blocks should be frequently renewed, and the blades of the rollers which gradually wear down, should not be permitted to become too short.

Machines called pulp refiners, now largely used in paper making, have recently been brought into use for the pulping of nitrocotton, their function being to complete the reduction of the fiber after it has been partially reduced in a pulper, a more uniform pulp being obtained and with less expenditure of power. These machines are of various forms. The Milne patent refiner, for example, consists of a central disc armed with a large number of bronze bars, which rotate between two stationary discs suitably armed. The arrangement is such that the pulp passes each cutting face in succession, being forced between the bars against centrifugal force. Coarse fibers are, therefore, thrown back again and retained until sufficiently reduced.

In the Hoyt hollander previously alluded to, the roller is placed at one end of a trough, and the material raised over the roller towards the back of the machine. The trough is divided by a cross section, reaching from the roller to almost the opposite end of the machine, into an upper and lower compartment. The rifling is placed in the deepest part of the trough, and the rollers are provided, according to the requirements, with straight or bent knives. The pulper has a very rapid circulation, so that the nitrocotton can be thrown in very thickly, and no sediment is formed. In the Hoyt-Horne pulper, the roller also lies at the end of the trough, and moves the material from the deepest part of the trough over the whole diameter of the roller towards the abruptly inclined neck, producing especially large falls for the movement of the nitrocotton. For this reason, and also on account of the favorable shape of the trough and the position of the rifling on the floor, a most efficient and rapid circulation is obtained.

The pulp trough is open, as in the old fashioned pulpers, and this is said to be of advantage in the constructon. There are nowhere places for dirt to settle or dead corners, and a washing drum can be installed in connection therewith. The roller is very wide in respect to the capacity of the trough, and thus the same effect is obtained as in pulpers with two smaller rollers, and requiring less power for transmission. The heavy cast iron roller is provided with strong knives, and possesses a powerful shaft running in oiled bearings, and provided with parallel shafting and releasing devices. These pulpers are furnished in three sizes; the front part near the roller together with the connection is always of iron, while the open trough in front can be made either of iron or of concrete.

A. Liedbeck[1] nitrates and grinds in one operation by means of a pulper provided with a hood to prevent acid vapors from escaping, the lower part of the pulper being provided with a cooling jacket for regulating the temperature during nitration. The nitrating mixture is first run into the pulper and the machinery set in motion. The cellulose is then added, in accordance with the progress of the pulping. As soon as the mass is sufficiently comminuted, it is run into the centrifuge, where the acid is wrung out. The nitrated cellulose is then washed in the usual manner.

In the J. Delpech method,[2] the nitrocellulose, after the usual washing process, is stabilized by treatment with superheated water in an autoclave. The water is circulated by means of a pump, and a mass of chalk, marble or the like, capable of neutralizing traces of acid present in the water or liberated during the treatment, is interposed in the circuit, in order to keep the water perfectly neutral and thus prevent hydrolysis of the nitrocellulose.

In the V. Voigt process,[3] the nitrocellulose is first freed from the nitrating acid, and then chopped up in a cutting machine, such as a forage or meat chopper, a paper cutter, or a planing machine, instead of, or in conjunction with the usual treatment

[1] U. S. P. 718484, 1903; E. P. 14690, 1897; 27397, 1898; F. P. 285488, 1899; D. R. P. 96109, 110289; Belg. P. 128925, 1897; Swed. P. 8049, 1896; abst. J. S. C. I. 1897, **16**, 656, 760; 1899, **18**, 401; 1903, **22**, 165; Mon. Sci. 1898, **52**, 94; 1899, **54**, 189; 1901, **57**, 29; Rev. Chim. Ind. 1899, **10**, 183; Chem. Centr. 1898, **69**, I, 1222; 1900, **71**, II, 231; Chem. Tech. Rep. 1898, **37**, 221; Jahr. Chem. 1898, **51**, 1382; Meyer Jahr Chem. 1898, **8**, 327; Wag. Jahr. 1898, **44**, 372; 1900, **46**, I, 397; Zts. ang. Chem. 1898, **11**, 167; 1900, **13**, 525.

[2] F. P. 441481, 1912; abst. C. A. 1913, **7**, 893; Chem. Ztg. Rep. 1912, **36**, 671.

[3] F. P. 470743, 474833, 1913; abst. Mon. Sci. 1916, **83**, 66; Chem. Ztg. Rep. 1917, **41**, 23; J. S. C. I. 1915, **34**, 199, 1118. D. R. P. 190073, 1905; abst. Chem. Zentr. 1907, **78**, II, 1881; Mon. Sci. 1910, **73**, 125; Chem. Ztg. Rep. 1907, **31**, 614; Wag. Jahr. 1907, **53**, I, 421; Zts. Schiess. Spreng. 1907, **2**, 435.

in beating engines. One could be facetious in commenting on this process. The J. Walton pulper[1] offers nothing new in connection with the pulping of nitrocellulose.

According to A. Colassi,[2] nitrocellulose intended for the manufacture of celluloid should undergo a process of stabilization with hot water if subsequent troubles are to be avoided, since even the most thorough washing with cold water is not sufficient to eliminate the unstable forms of nitrocellulose of a low degree of nitration. The material on coming from the hydroextractors or nitrating pots is ground in a hollander, and is afterwards repeatedly washed with successive changes of hot water until it is sufficiently purified to pass the heat test for stability. Two gm. of the nitrocellulose is placed in a test-tube and heated in a paraffin bath at 130°; a satisfactory material should not decompose with formation of brown fumes in less than an hour at this temperature. The occurrence of white points in celluloid is sometimes due to the presence of particles of nitrocellulose of a high degree of nitration; these white points are insoluble in alcohol and camphor, but may be recognized by their gelatinization in acetone.

A. Luck and C. Cross[3] stabilize by adding to the nitrocellulose an aqueous solution of zinc chloride. The "guncotton engine" of S. Mackie and C. Faure[4] is now mainly of historical interest.

Some firms construct what is known as an "auxiliary refining engine," the function of which is to take the nitrocotton from the pulper and reduce it to any fineness required in much less time than the regular pulper. This auxiliary refiner consists of an iron revolving disk with steel blades on both sides. This revolves between two other blades, one on each side, and by the action of the revolving disk the material is ground to the fineness

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1. U. S. P. 928009, 1909.

2. Caout. Guttap. 1918, **15,** 9604; abst. J. S. C. I. 1918, **37,** 686-A; C. A. 1919, **13,** 514.

3. U. S. P. 665792, 1901; abst. J. A. C. S. 1902, **24,** 51; Mon. Sci. 1901, **57,** 287. E. P. 18868, 1889. F. P. 282320; abst. Mon. Sci. 1899, **35,** 187. D. R. P. 117349, 1898; abst. Mon. Sci. 1901, **57,** 148; Chem. Centr. 1901, **72,** I, 288; Chem. Ztg. Rep. 1900, **24,** 93; Jahr. Chem. 1901, **54,** 895; Wag. Jahr. 1901, **47,** I, 492; Zts. ang. Chem. 1901, **14,** 117. Belg. P. 138487, 1898; 142091. Can. P. 86782. Ital. P. No. 90, **109,** May 31, 1899. Norw. P., May 10, 1899. Swed. P., May 8, 1899.

4. E. P. 2693, 1872; abst. Jahr. Chem. 1874, **27,** 1123; Chem. News, 1874, **29,** 166; Dingl. Poly. 1874, **213,** 174; Ber. 1874, **6,** 741.

required. To adjust the fineness, the two stationary plates may be brought closer together by means of a screw gear operated by the handle on the outside of the machine. The parts are interchangeable, the front and back plates and disk being replaceable. Excessive pulping increases the solubility of guncotton in ether-alcohol, while long treatment with even such feeble alkalis as calcium carbonate tends to hydrolyze cellulose nitrate.

Since the introduction of the very thorough system of purification by boiling, the original process of pulping as patented by J. Tonkin,[1] and three years later by F. Abel[2] has not the importance as a purification process as formerly. However, there is no doubt that with a long staple cotton the tubes contain impurities which are best and most readily removed by disintegrating the individual fibers, and pulping not only reduces the length of the fibers by breaking, but crushes them as well, so that impurities may be removed mechanically as well as by solvent action.

Irrespective of the apparatus used, method employed, or type of nitrocotton operated upon, as soon as the material has been reduced to the desired degree of fineness, the valve in the bottom of the pulper is opened, and the nitrocellulose in suspension allowed to flow away to settling rooms, as detailed in the succeeding topic.

Settling the Pulped Nitrocellulose. In some plants it is customary to run the pulped nitrocotton directly into settling rooms on a lower level than the beater, the rooms being lined with tin and having a floor also of tin containing many small perforations. There the pulped stock is allowed to settle, the water meanwhile running off through the perforations in the floor, in a manner similar to that employed in pulp and paper mills. Thorough draining is complete in 12 to 24 hours, depending upon the fineness to which the nitrocotton has been reduced, and the physical condition of the material. Whereas in the pulping process the ratio of nitrocellulose to water is usually about 1 to 10, after draining this has been reduced to about 1 to 1$^1/_2$, i. e., the former still contains about 150% of water.

In an alternate method, the properly pulped stock is pumped

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1. E. P. 320, 1862; abst. Mon. Sci. 1910, **72**, 728.
2. E. P. 1102, 1865; U. S. P. 59888, 1866; F. P. 69079, 1865 (Oct. 20), Addn. July 18, 1868. J. Roy, U. S. Inst. 1865, **8**, 345.

[redacted]

by means of centrifugal or other form of pump directly to the poachers where an additional purification and blending process takes place.

Poaching the Nitrocellulose. It being assumed that the operation of pulping has reduced the nitrocellulose to the required degree of fineness, the next operation is to wash out the impurities freed or "loosened up" by the previous processes to which it has been subjected. Poaching is designed to fulfil this, and at the same time to blend the material in a uniform manner.

The term poacher (also spelled potcher) is rather loosely defined, and strictly speaking, does not possess the same significance in Great Britain and on the Continent that it does in the United States. In Great Britain the poacher proper, shown in Fig. 220, consists of a large oblong iron trough with rounded ends, and with a central partition, somewhat like a hollander or beater, round which the pulp is circulated.

In the original form, a power-driven paddle wheel was used for circulating purposes, but in the larger and more recent types this has been replaced by a centrifugal pump. Fig. 221 shows the poachers as operated at Stowmarket, England. The poacher of this type being a flat vessel, careful adjustment of the parts in relation to the load carried is essential to ensure thorough and uniform agitation. The treatment in general consists in a series of washings with cold water, the pulp in each case being stirred up for a short time, allowed to settle, and as much water as possible removed by skimmers. In England a small amount of chalk is added as a stabilizer for nitrocellulose intended for the manufacture of cordite, being introduced in the last washing, when sufficient has not been deposited on the fiber during boiling from the natural alkalinity of the wash water used, or the chalk added.

The washing treatment may also be carried out in large vats or tubs called tuns, consisting of large cylindrical vessels of wood, or less often of iron, fitted with power-driven stirrers, and capable of holding 8,000 to 10,000 lbs. of guncotton. Considerable attention has been given by Nobel's Explosives Co. to the improvement of the stirring arrangement in these tuns. It has also been found that the ordinary strut form of stirrer gives very inefficient mixing, the proportion of nitrocotton to water at the bottom of the tun being very much greater than towards the top. This

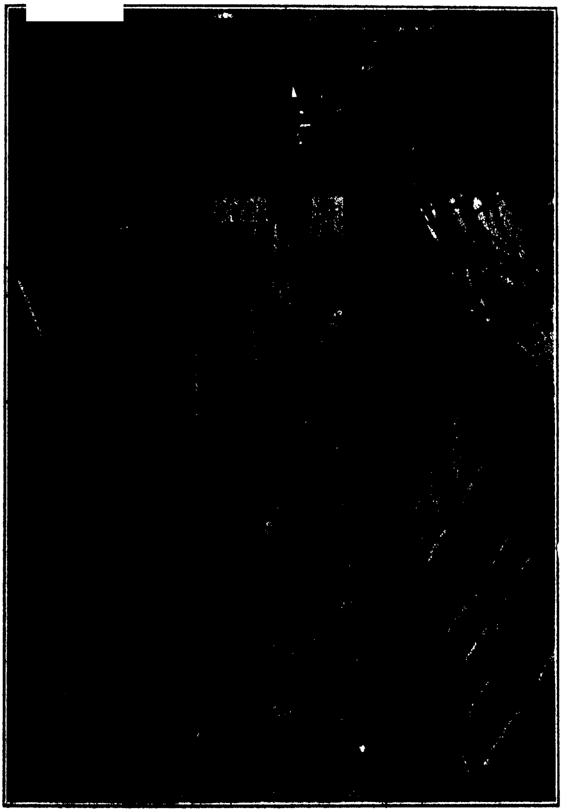

FIG. 221.—POACHERS OR TUNS, AS INSTALLED AT STOWMARKET

orm of stirrer has also the disadvantage that if the pulp is allowed o settle too long, it may be impossible to again start the stirrers. This difficulty has been overcome and almost perfect mixing obtained by the use of a stirrer shaped like a truncated cone, the mixing being promoted in a vertical direction, due to the difference between the circumferential speeds at the top and bottom of the cone.

In the case of poacher washing, as the poacher holds but about 2,000 lbs. of nitrocellulose, it becomes necessary, in order to obtain a uniform blend and efficient washing, to transfer the washed pulp to separate blending vessels. Large iron tanks are used for this purpose. An installation of centrifugal pump poachers and blending tuns is illustrated in Fig. 222.

The poachers in use at Waltham Abbey hold about 1,000 lbs. nitrocotton, and about 1,100 gal. of water, and are equipped with power-driven paddles for agitation purposes. The nitrocotton receives at least three washings, being allowed to settle after each washing, and the wash waters removed. The wash water contains in suspension foreign bodies of a lower specific gravity than guncotton, and in the first washings, there is always present a scum containing nitro-bodies of low stability.

Practice in various countries, and with manufacturers in the same country differs widely as to whether the poaching treatment is confined to a series of cold water washings, followed by washing with water near the boiling point in the same or different containers, or whether the poaching is entirely conducted in one series of vats and hot water only used. Where sufficient equipment and capacity is at hand, the most approved practice appears to be to simultaneously pump the contents of several pulpers into the same poacher, the latter being made of maximum capacity for economical manipulation, in order to obtain, incidentally, a blending of maximum uniformity. Usually the poachers are made of a minimum capacity to take the contents of at least four beaters each. By arranging the poachers in series of two pairs with sides touching, and locating the pumping mechanism so that it is in the center and above the tops of the four round poaching vats, and by providing a device whereby the pulped nitrocotton is made to flow into each poacher uniformly during the pumping operation, it is possible to evenly distribute some

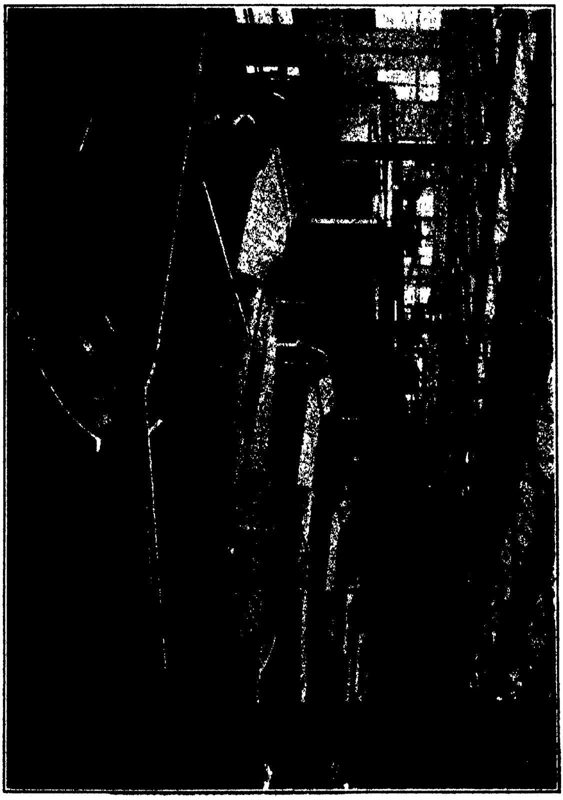

FIG. 222.—INSTALLATION OF CENTRIFUGAL PUMP POACHERS AND BLENDING TUNS (NOBEL'S EXPLOSIVES CO.)

of the contents of thirty-two beaters in a single poacher.

The most approved practice in the United States is to pump directly the contents of the beaters into poachers. In Fig. 223 is shown a row of 24 of the 48 poachers installed at the Old Hickory plant of the du Pont Co., each of capacity of over 10,000 lbs. nitrocotton, and of a total capacity, therefore, of one-half million pounds. The water used for poaching, may, or may not contain a trace of sodium carbonate. The poacher is sometimes referred to as a "stuff-chest." From the poaching operation, the now neutral and sufficiently stabilized pulp is either screened, as by a Packer screen, or passed over blankets to remove inorganic impurities and insufficiently beaten fibers, and continue the blending operation.

The blending up to this point has been very thorough. As indicative of its efficiency, F. Nathan[1] has reported that in 1907–1908, of 291 tests representing 600 long tons of nitrocellulose produced, the nitrogen varied but from 12.93% to 13.05%, with a mean of 13.0195%.

As judging of poacher capacity, the following is a concrete example: Sixteen poachers, each 9′ x 11′ high, round, in a battery of four rows of 4 each, driven by shafting at the bottom between the first and second rows, and the third and fourth, may be run by two motors, each form K, cycle 60, h. p. 69, volts 440, speed number of load 600, full load 575. For pumping the pulped nitrocellulose to the poachers, there is required h. p. 5, volts 440, amperes 6.7, phase 3, frequency 60, r. p. m. 1150.

The piping system from pulper to poachers, and from the latter to the dehydrating centrifugals, should be so arranged for the maximum of blending effect that the contents of any beater may be pumped to any poacher, and from any one of the latter, to any of the dehydrating wringers.

Removal of Foreign Matter. The comminution of the nitrocotton incidental to pulping has mechanically separated insoluble siliceous and metallic particles of greater density than the nitrocellulose, and it is customary to provide some mechanical

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[1] J. S. C. I. 1909, **28**, 177, 181; abst. C. A. 1909, **3**, 1342; Chem. News, 1909, **99**, 83; Bull. Soc. Chim. 1910, **8**, 60; Mon. Sci. 1910, **72**, 111; Rep. Chim. 1909, **9**, 376; Chem. Zentr. 1909, **80**, I, 1678; Chem. Ztg. 1909, **33**, 208; Chem. Ztg. Rep. 1909, **33**, 146; Jahr. Chem. 1909, **62**, II, 388; Meyer Jahr. Chem. 1909, **19**, 333; Wag. Jahr. 1909, **55**, I, 431; Zts. ang. Chem. 1909 **22**, 1614; Zts. Schiess. Spreng. 1909, **4**, 285, 327.

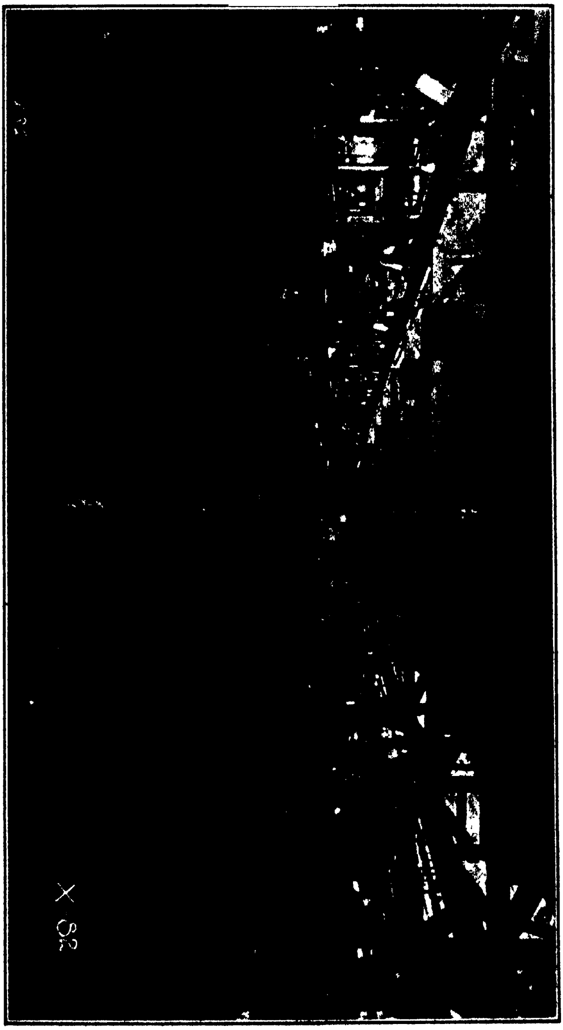

FIG. 223.—POACHER HOUSE (E. I. DU PONT DE NEMOURS CO.)

arrangement in order to remove from the pulped material any particles of grit, iron or other extraneous matter.

This mechanical purification is usually brought about by suspending the nitrated cotton in a large bulk of water, in which condition it may be run through what is known as grit traps, placed at convenient intervals in a long, shallow trough, preferably of concrete, the bottom of which is covered with blanket. Such an arrangement is shown in the photograph in Fig. 224, being the arrangement as installed at Nobel's Explosives Co. plant at Ardeer, Scotland, and together with Fig. 225, reproduced herewith through the courtesy of this Company.

Any foreign matter, such as sand or pieces of metal picked up in the normal course of manufacture, would be a source of danger at a later stage when the nitrocotton is dry and sensitive to friction. Trays fitted with spikes are also placed in the chutes, and are useful for retaining long fibers which have partially escaped pulping. In some factories straining machines are employed for this purpose, as explained in the succeeding topic. It will be observed by reference to the photograph that the chutes have bars laid across them at frequent intervals, these bars acting as grit traps to retain foreign matter.

The pulp is then passed over electro-magnets as shown in Fig. 225, being in the form of knobbed bars for the elimination of finely divided iron, after which the nitrocotton is ready for washing.

Some factories use a contrivance known as a "knotter," being an appliance to remove small knots or large pieces of imperfectly pulped nitrated material. This is in addition to the grit traps, electro-magnets and rocking screen, through which the pulped mass is passed before centrifugal dehydration.

If the nitrated cellulose is to be used for transparent solutions as lacquers, bronzing liquids, or for the formation of artificial silk or similar filaments, where it is necessarily subjected to a careful filtration before use, the previously described refinements are not as necessary because of the thorough filtration to which the pyroxylin solution is subjected before use.

Where the nitrated cotton is to be used for smokeless powder and similar explosive compounds, especially for small arms or shoulder ammunition, subsequent filtration of the colloid cake

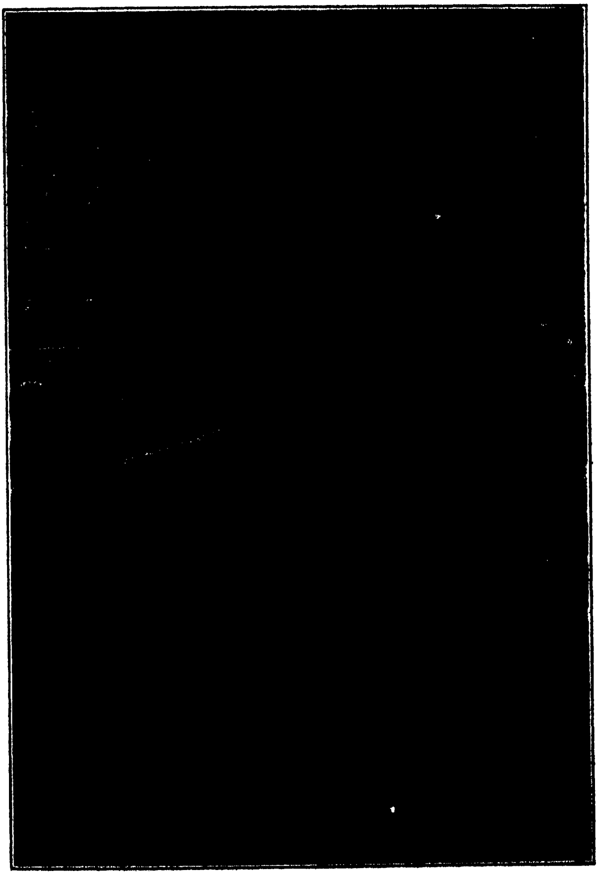

Fig. 224.—Chutes for Removing Foreign Matter (Nobel's Explosives Co., Ardeer, Scotland)

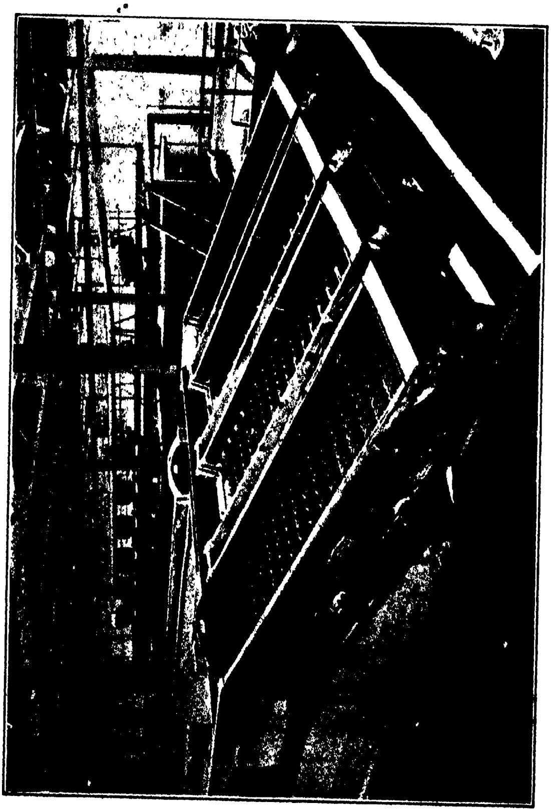

Fig. 225.—Installation of Electro-Magnets (Nobel's Explosives Co., Ardeer, Scotland)

through the macaroni press as described in Volume VII is supposed to remove all the larger insoluble matter, but does so only with those particles larger than the mesh of the sieve in the macaroni press, and does not effectually remove particles of a diameter under 0.5 mm.

Blending. During the entire series of operations for the purification of the cellulose, blending is unwittingly made, and also from the nitration of the cellulose through preliminary boiling, beating, poaching and centrifugal dehydration, the thorough agitation to which the fibrous and pulped nitrocellulose is necessarily subjected, usually results in an intimate blending. The process of pulping, especially produces a uniform product up to the capacity of an individual beater. Poaching carries on this blending in a more systematic manner, especially where the contents of several beaters are distributed into a number of poachers, and also in larger amounts at a time, the usual size of beaters used being equivalent to but 1000 to 1500 lbs. of dry nitrated cotton.

In those applications, however, in which solubility, viscosity, nitrogen content and stability are required to be brought to a definite and uniform standard, the nitrocotton is usually subjected to a separate and distinct process of blending, immediately preceding the final centrifugal dehydration. When the nitrocotton is intended to be used in the fluid state, satisfactory blending may be attained by dissolving the material in large containers, either with or without mechanical agitation, but usually with the latter.

It is customary after stabilization, for viscosity and stability determinations to be made, from which the use of the product to fulfil certain technical requirements is determined. From the results obtained, definite amounts of various nitrocelluloses may be mixed in proportions indicated by the analysis, to produce mixtures of pre-determined constants. In this manner, nitrogen percentage, stability, viscosity and solubility may be adjusted within comparatively narrow limits, and increased uniformity thereby resulting, even although quite dissimilar nitrocelluloses may have been used.

While not required by the U. S. army pyrocollodion powder, there are many grades of guncotton used for military purposes which require a final mixing or blending of not less than 6 to 10 poacher lots, this blending to immediately follow the poaching and the mechanical removal of impurities. This blending, of course, is performed for the sole purpose of securing greater uniformity in the nitrocotton as determined by the various tests in the laboratory to which the material has been subjected, for it is upon the results of these tests that the nitrocotton is accepted or rejected for the particular purposes intended. Individual poacher lots showing tests which place them outside of the specifications, can still be made to fall within the requirements by judicious blending. A series of four blenders joined in one is shown in Fig. 226, the capacity of each being about 100,000 lbs. and hence of a capacity of 10 to 15 poachers. In making a blend, the piping and pumping arrangements are usually such that the contents of one poacher may be pumped into one or more blenders at the same time, this being accomplished by means of a central pipe located at the top of and between the blenders.

The nitrocotton from the poachers, still containing the final wash water, is run in the blenders by means of centrifugal pumps electrically driven, the agitators in the blenders having been started a few minutes previously to prevent a settling of the nitrocotton and thus causing jamming. The scheme of propulsion, is indicated in Fig. 227. Nitrocotton in suspension is continually pumped into the battery of four blenders until the latter are full, agitation being meanwhile continued, at about 45 r. p. m. A sample for analysis should not be taken until the blender has been run to full capacity for at least one hour, and a more advizable practice seems to be to take three samples, one at the beginning, one after one hour's agitation, and the third just before the blender agitators have been shut down. The total time of running the blender will vary from two to six hours, or even more, depending in a great measure upon the speed of pumping from poacher to blender, and the number of the former which are installed. Blending is preferably continued until after the analysis of the sample withdrawn has been completed, for sometimes it is found that after the tests have been made, another poacher contents is required in order to meet the specifications. From the blender, the stock is transported to the dehydrating centrifugals, now having been proven by physical test and chemical

Fig. 226.—Nitrocellulose Blenders. (The capacity is indicated by the comparative size of the man on the platform at the left)

analysis to meet the specifications which have been imposed upon it.

It is customary to erect the dehydrating centrifugals at such elevations that the bottom discharge empties directly into a metal-lined receptacle which is usually a large room, with a capacity of several tons. The nitrated cotton carrying from 30% to 35% of water and being in a finely divided condition can be thoroughly mixed in such a room by hand by means of wooden, so-called, "potato" shovels. If intended for smokeless powder use, from this room it is weighed out in such amounts that one batch will completely fill an alcohol hydraulic displacement press, placed in zinc or tin-lined wooden boxes preferably with her-

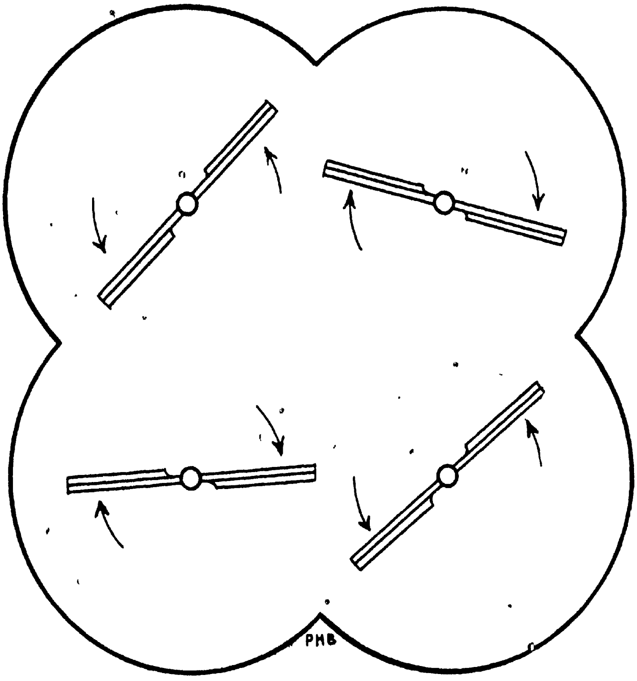

FIG. 227.—PLAN OF NITROCELLULOSE BLENDERS, SHOWING STIRRING ARRANGEMENTS

metically sealed covers, and stored in an adjacent building until required.

In 1897, A. Liedbeck[1] obtained patent protection for a process intended to obviate the disadvantage of want of uniformity resulting from the ordinary methods of nitration, by allowing the beating or pulping and nitration to proceed simultaneously. In his preferred method, the acid mixture is introduced into the beater which is then set in motion, the cellulose being introduced by degrees preferably through a feeding aperture in the hood until the whole quantity of cotton weighed off has been introduced. When the mass has acquired the fineness desired it is then freed from excess of acid centrifugally and washed to neutrality in the usual manner. It is evident that in this process, as described, there must be a large loss of cotton, both by solution in the nitrating mixture and in subsequent washing, while the ratio of acid to cotton must be great in order that the last portion of cellulose immersed may be reacted upon by nitrating acid of practically the same composition as the first portion. So far as aware, this process has never attained commercial prominence.

The International Smokeless Powder & Chemical Co.[2] have obtained patent protection for the idea of blending nitrocelluloses of varying solubility and nitrogen content, by dissolving them separately in the solvent or solvent mixture especially suitable to each, then mixing together the resulting solutions, and obtaining the nitrocellulose therefrom by removal of the solvent.

In the method as described by A. Nobel and A. Liedbeck[3] solutions of nitrocellulose or nitrostarch are evaporated in very thin layers on a rotating drum or the inner cylindrical surface

[1] U. S. P. 718484, 1903; E. P. 14690, 1897; 27397, 1898; F. P. 285488, 1899; D. R. P. 96109, 110289; Belg. P 128925, 1897; Swed. P. 8049, 1896; abst. J. S. C. I. 1897, **16**, 656, 760; 1899, **18**, 401; 1903, **22**, 165; Mon. Sci. 1898, **52**, 94; 1899, **54**, 189; 1901, **57**, 29; Rev. chim. ind 1899, **10**, 183; Chem Centr. 1898, **69**, I, 1222, 1900, **71**, II, 231; Chem. Tech. Rep. 1898, **37**, 221 Jahr. Chem. 1898, **51**, 1382; Meyer Jahr. Chem. 1898, **8**, 327; Wag. Jahr. 1898, **44**, 372; 1900, **46**, I, 397; Zts. ang. Chem. 1898, **11**, 167; 1900, **13**, 525.

[2] D. R. P. 179634, 1903; abst. Wag. Jahr. 1907, I, 477; Zts. ang. Chem. 1907, **20**, 1195; Chem. Zentr. 1907, I, 1475; Chem. Tech. Rep. 1907, **31**, 32; Chem. Ind. 1907, **30**, 50; Zts. Schiess. Spreng. 1907, 12; C. A. 1907, **1**, 2202. E. P. 13457, 1903; abst. J. S. C. I. 1903, **22**, 963; Arms and Explos. 1903, **11**, 144; Chem. Ztg. Rep. 1904, **28**, 1030. E. P. 23252, 1901; abst. Arms and Explos. 1901, **9**, 63. Can. P. 84502, 1903. U. S. P. 781926, 1905; abst. Mon. Sci. 1905, **62**, 142; J. A. C. S. 1905, **27R**, 588.

[3] Swed. P. 9773, 1897; abst. Chem. Ztg. 1899, **23**, 550; Chem. Tech. Rep. 1899, **38**, 196.

of a rotating centrifuge, the evaporation of the solvent being aided by a current of warm air. Care must be taken not to add more solution until the previous layer is perfectly dry, an entirely homogeneous powder resulting. The claim is made that powder suitable for the largest cannon can be thus produced and that the powder contains no pores and no residual solvent. The above process has been modified[1] by first forming films of lower nitrated material containing 10% N, upon which a layer of 13.5% N nitrocellulose is deposited, a final layer of the lower nitrated product being superposed. The films thus obtained are used either as spirals or small leaves.

Screening the Pulped Nitrocellulose. Either in conjunction with, but more often as a substitute for, the processes for removal of foreign impurities mentioned in the preceding topic, is the employment of some form of diaphragm screen for mechanically separating the properly pulped material from that which has not been sufficiently subdivided. The pulped nitrocotton suspended in a large volume of water is run over sieve bars to which a rocking or oscillatory movement has been imparted, whereby the finer particles are sifted in a wet condition, and the coarser product is caught, to be returned and retreated.

The photograph of the Downingtown diaphragm pulp screen shown in Fig. 228 is what is known as a "12 plate" screen, in which there are 12 bronze plates 12" wide and 42" long. The machine consists of a vat in which the plates are fastened; a frame on which the vat is mounted; a flow box fastened to the frame; cast iron open side end frames, and a connecting girder extending from the end frame to end frame on which the bearings for the screen shaft is mounted. The vat is constructed of 3" cypress lumber bolted together, and having oak cross bars for supporting

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[1] Swed. P. 9775, 1897. D. R. P. 97690; abst. Wag. Jahr. 1898, **44**, 370; Chem. Centr. 1898, **59**, II, 687; Chem. Ztg., 1898, **22**, 565; Zts. ang. Chem. 1898, **11**, 676; Mon. Sci. 1898, **52**, 266. H. Maxim (E. P. 16858, 1896; F. P. 267814, 1897; abst Mon. Sci. 1897, **49**, 510; 1898, **52**, 187; Rev. chim. ind. 1898, **8**, 374; Chem. Ztg. 1898, **20**, 558; Jahr. Chem. 1897, **50**, 1509; Meyer Jahr. Chem. 1897, **7**, 301) has described a method of blending of the finished nitrocellulose, in which fibrous guncotton is made into paper, the surface of the paper is then made adhesive, and a number of sheets are pressed together to build up the explosive. The paper may be still further blended by being made from a mixture of guncottons of different solubility and nitrogen content, the more soluble being dissolved before the compression of the sheets. The sheets are finally cut into strips or squares to produce the finished powder.

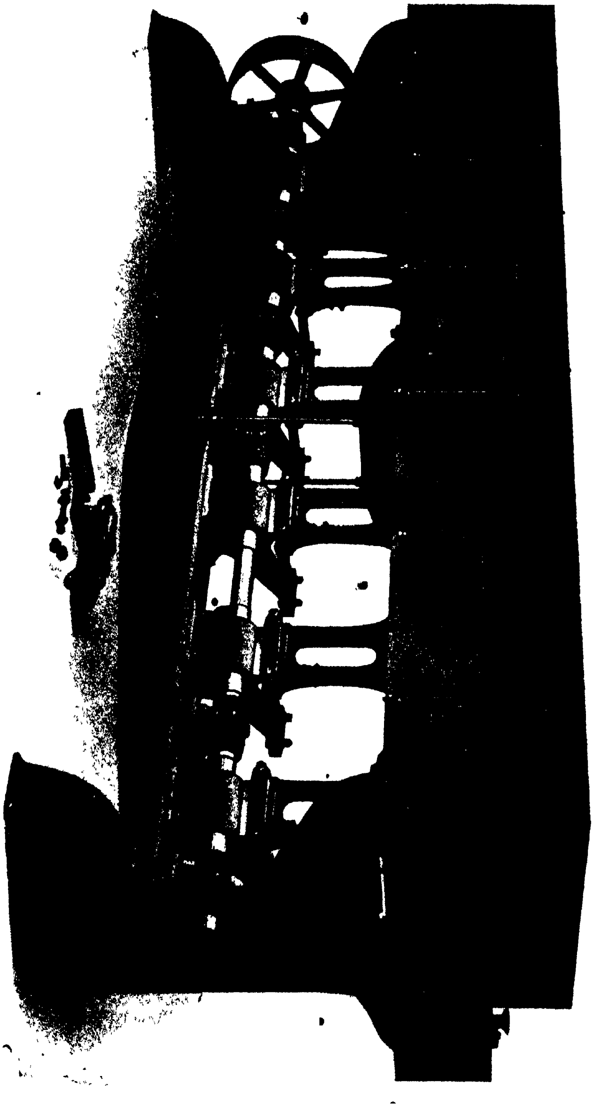

FIG. 228.—THE DOWNINGTOWN PULP SCREEN

the screen plates. The vat frame is of yellow pine bolted together, and having cross timbers to which the diaphragms are fastened.

For ready accessibility to the diaphragms, the vat is provided with swing bolts and hinged locking clamps as shown in the photograph. The diaphragms are of 5-ply rubber and cotton duck, securely fastened to the vat frame and clamped to the oak diaphragms attached to the pitmans. These latter are connected to diaphragm at top and ride on cams. The pitman shoes are compelled to follow the cams by means of springboards, made adjustable with spiral springs and hand nuts. This construction ensures smooth running with a minimum of noise.

The screen is provided with a flow box of cypress, and equipped with adjustable flow boards to insure even flow of screened stock. The screen plates are of bronze, 12" x 40" x $^5/_{16}$" thick, with slots 0.006". Witham screen plate fastners are furnished when called for.

Another type used extensively in the screening and separation of impurities from pulped nitrocellulose is the J. Packer's open side, sectional diaphragm screen,[1] as made by the Sandy Hill Iron and Brass Works, Sandy Hill, N. Y., being constructed of cast iron open side end frames connected by cast iron girt bolted to the end frames, and provided with two $^{15}/_{16}$" steel cam shaft, with cams of $8^1/_2$" face, keyed to shaft, for operating the diaphragms. This machine is shown in Fig. 228. Of especial interest in connection therewith, is the G. Witham screen plate fastener[2] illustrated in Fig. 229, with one of the screen plates enlarged, detailed in Fig. 230. The stock pulped in a thin paste by means of a large bulk of water, is flowed over this vat with screen plates in motion, thus filtering the finely pulped nitrocotton, while the grit, and larger particles pass on. An arrangement of this nature is very efficient for this purpose, being capable of expeditiously handling a large amount of material without recleaning.

Dehydration of the Nitrocellulose. The properly pulped nitrocotton, poached until the desired stability has been attained, as shown by laboratory examination, the improperly or incompletely pulped fibers eliminated by screening, the iron removed by electromagnets, and the silica and other extraneous impurities also removed by means of grit traps or by blankets, it then only remains to deprive the nitrated cellulose of the water as far as possible by purely mechanical means, or aided by solvents, when the balance of the moisture is removed by drying, and the product is ready for use in the arts. Dehydration of nitrocellulose is accomplished on a factory scale in one of the four following ways:

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[1] U. S. P. 669933, 1901.

[2] U. S. P. 678082, 1901. See also G. Witham, U. S. P. 680514, 1901, for cleaner for paper pulp screens.

1. Centrifugalization, followed by drying.

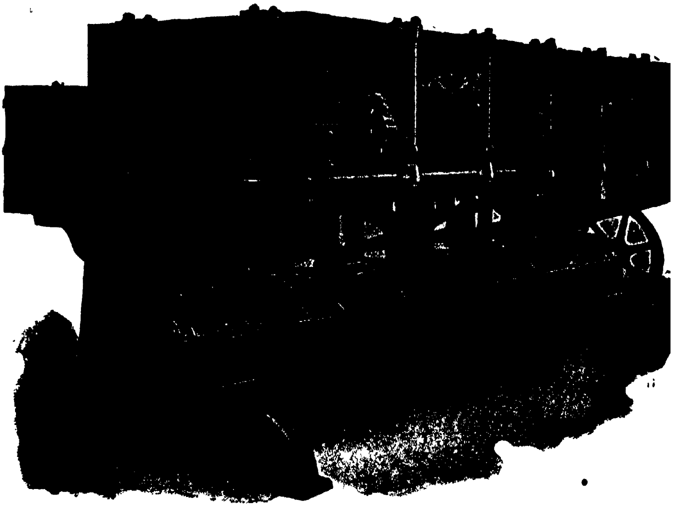

FIG. 229.—PACKER'S OPEN SIDE SECTIONAL DIAPHRAGM PULP SCREEN

2. Centrifugalization, then displacement of water by alcohol or other water miscible cellulose nitrate non-solvent, the entire process taking place in the centrifugal.

3. Hydraulic dehydration. More efficient than simple centrifugal dehydration, i. e., a larger proportion of the contained water is removable.

4. Hydraulic solvent dehydration. Displacement of the major portion of the water remaining after hydraulic pressure, by the introduction of ethyl alcohol, and further hydraulic pressure. In practice, wherever process three is employed, the next process

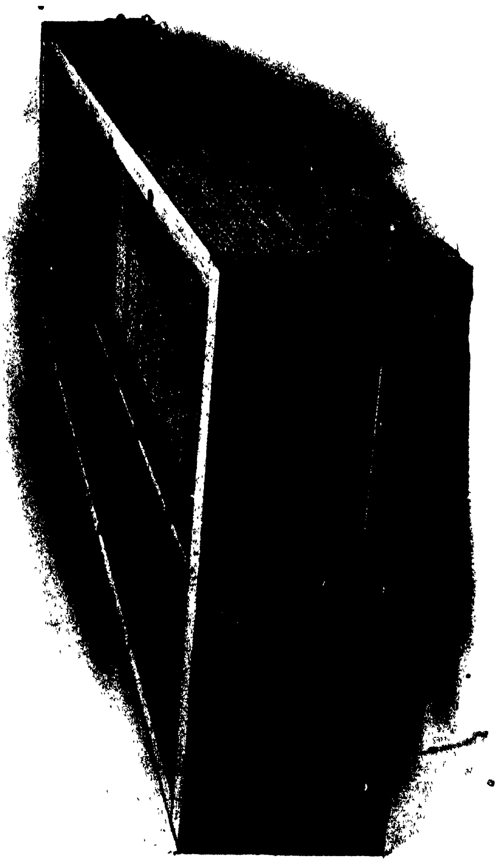

Fig. 230.—Union-Witham Screen Plate Vat and Fastener

is used in conjunction with it.

Processes two or four (the employment of alcohol), are much the superior to simple water elimination, because the alcohol actually dissolves and removes lower nitrated celluloses of deficient stability. Therefore solvent dehydration increases the stability of the nitrated cellulose. This repeatedly has been proven by vacuum evaporation of the alcoholic extract and determining the nitrogen content and stability of the nitrated cellulose esters contained therein. In the manufacture of pyrocollodion smokeless powder, the alcohol will normally dissolve from 1%–3% of bodies, of an average nitrogen content seldom exceeding 10%.

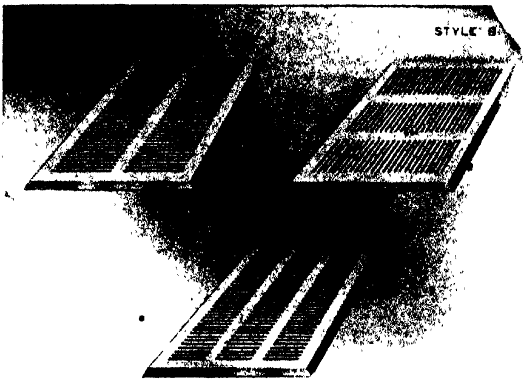

FIG. 231.—WITHAM SCREEN PLATES

The above processes are described in the immediately succeeding topics.

Centrifugal Dehydration. But a relatively small proportion of the nitrocellulose used industrially is dried before use, chiefly on account of the additional time and expense involved, and also because of the danger attended by depriving the pyroxylin of the balance of contained moisture, and the inconvenience of transporting dry nitrocotton. In employing it in the moist state, there is not only a considerable saving of time between manufacture and use, through elimination of the drying process, which at the low temperature required (25°–35°) necessitates several days, but the danger in handling and transportation of nitrocellulose is materially diminished where the latter is kept continually moist, and in the majority of countries the transportation of nitrated cotton is prohibited except in very small quantities, unless containing a minimum percentage of water.

The usual method, after continued washing has resulted in a nitrocellulose of acceptable stability, is to remove the bulk of the water contained in the pulp, by means of a centrifuge, lined with fine canvas. The damp mass thus obtained contains from 32% to 45% of water, depending upon the speed of the centrifugal, and the length of time of the wringing process. At the end of the wringing, the nitrocotton is tightly packed against the sides of the rotating basket. By placing a rope, encased in cloth to prevent particles of the rope contaminating the product, around the inside of the basket, at the close of the wringing operation, the rope may be readily detached, bringing the packed product with it. It is customary in this process to employ a centrifugal with bottom discharge, the Tolhurst wringer shown in Fig. 232, and in section in Fig. 233, being largely used in the United States for this purpose.

This extractor is made in 32, 40, 48, 54, 60 and 72 inch sizes and is self-balancing, being provided with "griddle" bottom discharge. The centrifugal has two openings in the bottom of the basket, and one opening in the case, through which the load is discharged after centrifuging. The wringer may be countershaft, motor or engine driven. After the moisture has been removed from the material, the lid is raised, and the load falls down into the waiting receptacle, thus doing away with the necessity of shoveling it out. The basket bottom is of a special grade of soft, but strong and tough cast iron. As a final purification treatment, the centrifugal may be provided with a spray nozzle, consisting of a finely perforated 40 mm. pipe, arranged for properly spraying the nitrocotton, the pipe being permanently attached to the back part of the case cover.

A battery of centrifugal dehydrating machines with bottom discharge, as installed at the Ardeer factory of Nobel's Explosives Co., is shown in Fig. 234.

In the centrifugal as patented by F. Kaehl,[1] the drum of the machine is formed of two frusto-conical sections connected together at their largest peripheries by a perforated ring, and mounted by a "spider" on a vertical shaft, by which the drum can be rotated within a casing. The upper opening of the compound drum is larger than the lower, through which the material to be separated is fed by a pipe. The separated liquid portion flows away over the edge of the upper opening, and the solid matter is removed from the interior surface of the drum by stationary scrapers, carried by a sleeve which fits over the central shaft, and is discharged through the perforated ring which connects the upper and lower halves of the drum together.

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[1] U. S. P. 840497, 1907; abst. J. S. C. I. 1907, **26**, 307.

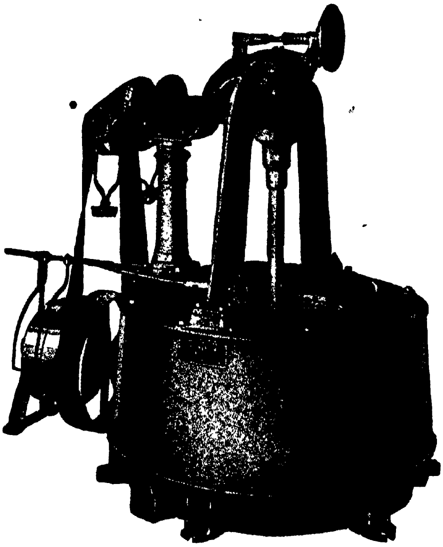

FIG. 232.—SECTIONAL VIEW OF TOLHURST BOTTOM DISCHARGE EXTRACTOR

In the employment of centrifugal wringers for this class of work, the fact should be borne in mind that the number and size of the perforations, and the distance between centers of the holes, has much to do with the relative efficiency of the apparatus, the amount of water which may be expelled in a given period of wringing at a pre-determined speed, and hence with the volume of nitrocellulose which may be dehydrated efficiently in a given time. This in turn depends in a large measure upon the physical state of the nitrocellulose, especially as to the degree of nitration to which the cellulose has been subjected, and the fineness with which it has been beaten in the pulpers.

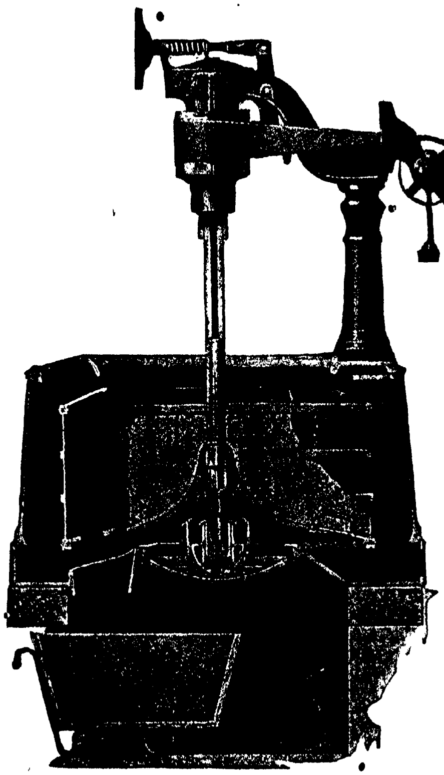

FIG. 233.—TOLHURST SELF-BALANCING DEHYDRATING CENTRIFUGAL

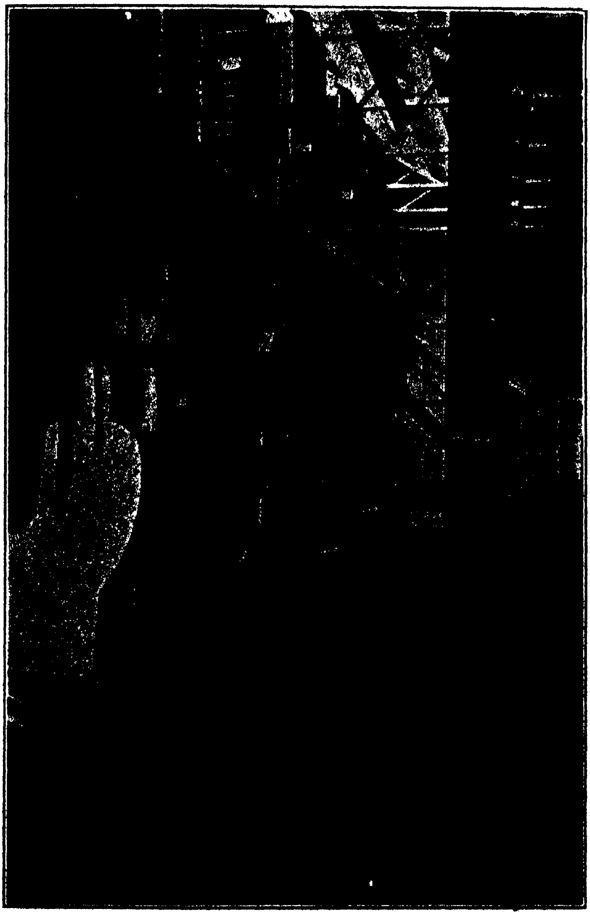

FIG. 234.—INSTALLATION OF CENTRIFUGAL MACHINERY (BOTTOM DISCHARGE) AT ARDEER FACTORY, NOBEL'S EXPLOSIVES CO.

Where a nitrocellulose of one kind or method of nitration is produced in large amounts for a considerable period, the above factors should be taken into careful consideration in the selection of the kind of centrifugal best adapted for dehydration purposes, especially as to the number, size and arrangement of the basket perforations. Too large perforations mean a more rapid moisture elimination, but also a considerable increase in loss of fine nitrocellulose, whereas too small perforations, while it diminishes mechanical loss of finely comminuted nitrated cellulose, also diminishes the output per machine.

T. Irwin,[1] and A. Dunsmore[2] have also described centrifugals suitable for this purpose.

With the A. Robertson apparatus,[3] the dried material is discharged from the basket of a centrifugal machine by a scoop device which projects from a hub surrounding the central shaft. When the machine is ready to be discharged, a brake is applied to the hub before the rotation of the drum is stopped, so that the scoops move relatively to the drum and detach the lower portions of the deposit, whereupon the remainder easily falls away.

H. Edenborough,[4] H. Broadbent,[5] and H. Fearnley[6] have patented centrifugal wringers adapted to the removal of water from nitrocotton. The efficiency of these centrifugals is directly proportional to the radius of the machine, and to the square of the angular velocity.[7]

According to F. Crane[8] premature explosion of wet guncotton in centrifugal driers is prevented by suddenly reducing the pressure within the receptacle surrounding the centrifugal wringer when the moisture content of the nitrocotton has been somewhat reduced by centrifuging. This sudden reduction of pressure is said to cause rapid vaporization of the moisture remaining in the guncotton, and thus serves to cool it, and loosen up the mass.

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[1] E. P. 13508, 1913; abst. J. S. C. I. 1914, **33**, 1041.
[2] E. P. 12062, 1910; abst. J. S. C. I. 1911, **30**, 407.
[3] E. P. 8306, 1914; abst. J. S. C. I. 1915, **34**, 15.
[4] E. P. 21947, 1912; abst. C. A. 1914, **8**, 1029; J. S. C. I. 1913, **32**, 954. It is claimed that a drying centrifugal of 42" diam. at 900 r. p. m. will give a uniform pressure throughout the mass of 500 lbs. per square inch. Using a 42" basket centrifuge at 1350 r. p. m. the nitrocellulose moisture may be reduced to 16% water. Such a centrifuge should be surrounded by ferroconcrete as protection to the workmen.
[5] E. P. 8376, 1913; abst. J. S. C. I. 1914, **33**, 582.
[6] E. P. 25849, 1912; abst. J. S. C. I. 1913, **32**, 1104.
[7] C. Rivière and L. Clement, Mat. Grasses, **3**, 1896; abst. C. A. 1910, **4**, 3124.
[8] U. S. P. 1295089, 1919; abst. C. A. 1919, **13**, 1152; J. S. C. I. 1919, **38**, 604-A.

The continuous action centrifugal hydro-extractor of Soc. Leflaive et Cie,[1] shown in Fig. 235, comprizes a number of planetary baskets, *5*, mounted on shafts, *4*, which have bearings in cross-pieces, *2*, *3*, carried by a central shaft, *1*. The shaft *1* is driven by a pulley, *22*, and the shafts *4* are driven slowly by epicyclic gearing, *9*, *10*, *11*, *12*, the teeth *12* being on the base-plate *6*. The material is fed to the baskets by a distributor, *15*, on the shaft *1*. The discharge liquid is collected in a trough, *16*, and the dried solids are forced by scrapers, *18*, driven by gearing, *19*, *20*, into a chute, *21*.

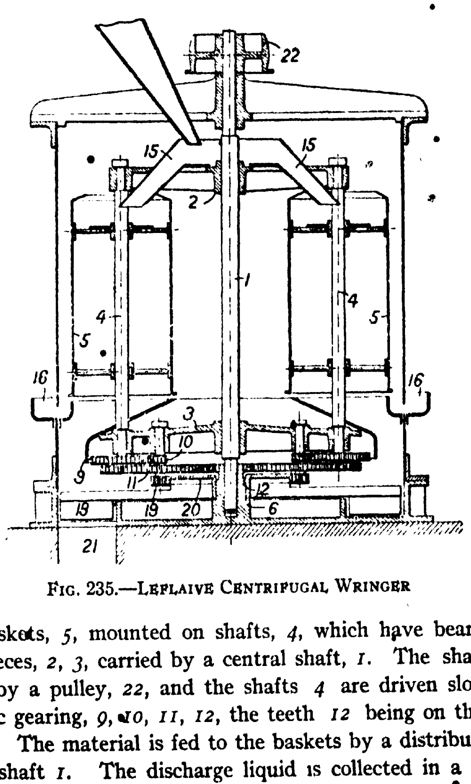

FIG. 235.—LEFLAIVE CENTRIFUGAL WRINGER

The centrifugal extractor of F. Müller[2], shown in Fig.

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[1] E. P. 2753, 1912.
[2] F. P. 408082, 1909.

236, has been put forward as especially valuable for the handling of nitrocellulose.

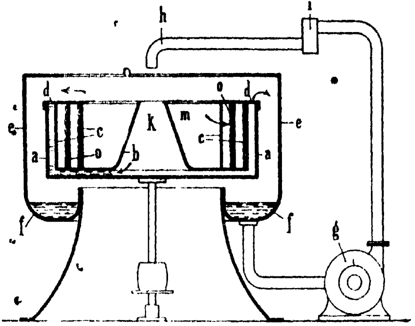

FIG. 236.—THE MÜLLER CENTRIFUGAL EXTRACTOR

Centrifugal Solvent Dehydration. In any method of replacement of water by a constituent present in the finished nitrocellulose preparation—and all fluids for this purpose must be such as enter into the final use to which the nitrocotton is to be put—the fluid used to eventually replace the water, must at least fulfil the following two conditions:

1. It must be miscible or nearly so with cold water in the proportions required to effect the degree of dehydration desired, and must also be a normal constituent present in the formula in which it is intended to use the pyroxylin.

2. It must be a sufficient non-solvent not to gelatinize or cause incipient colloidation of the nitrocotton, for if it does, then the water is removable with difficulty, or not at all. Furthermore, the heat of combination with the water to be removed must not be unduly high.

The above generalizations preclude the use of any of the pyroxylin solvents miscible with water without turbidity, although A. Durnford[1] has suggested the use of acetone as the dehydrating agent. However, in proceeding according to the prescribed process of the patentee, the cellulose nitrate is left as a putty-like mass, difficult to handle or subdivide. About the only bodies which have been found efficient for this purpose, therefore, are ethyl alcohol, or the first runnings in the rectification of crude fusel oil, and consisting primarily of propyl alcohol. This latter, although often producing an emulsion with water, is efficient for the purpose, and to be recommended when the nitrocotton is to be employed for pyroxylin lacquers, bronzing fluids or waterproofing solutions.

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[1] E. P. 20880, 1892; abst. J. S. C. I. 1892, **11**, 1056; 1893, **12**, 890, 949. E. P. 3578, 1886; abst. J. S. C. I. 1887, **6**, 226; Wag. Jahr. 1887, **33**, 569.

Ethyl alcohol at the present time, however, is almost universally used, especially in the manufacture of smokeless powders, where it is afterwards colloided by the addition of ethyl ether thereto. Where ethyl or propyl alcohols are used, the nitrocotton can readily be disintegrated by the hand—i. e., it is not sticky.[1]

The alcohol is sprayed into the centrifugal during motion, and after the maximum of moisture has been removed by rotation alone, wringing is continued until the density of the alcohol-water running out of the centrifuge has a gravity corresponding to a known proportion of alcohol and water, when the spray of alcohol is turned off, and wringing continued until no more fluid leaves the wringer. The nitrocellulose is then removed as quickly as possible to minimize loss of alcohol by evaporation, and placed in weighed amounts in air-tight containers, usually zinc lined. In any alcohol dehydrating process, the alcohol recovered is subsequently rectified for use again.

A predetermined amount of alcohol is always added, the amount used being calculated by previous experimentation.

The Elektro-Osmose A. G. has taken out a series of patents[2] for the displacement of liquids in nitrocellulose by other fluids by the aid of electro-osmosis, in which the material to be treated is subjected to the action of the electric current between electrodes, the displacing liquid being introduced at one electrode and the displaced liquid removed at the other. The material is separated from the electrodes by diaphragms. The process is accelerated by the use of electrolytes, viz., by those containing OH-ions if the liquid moves towards the cathode and by those containing H-ions if it moves towards the anode. In displacing water from nitrocellulose by alcohol, for example, alcohol is fed in at the anode, and the displaced water collects at the cathode, both electrodes being perforated. The cellulose bodies for which the process is particularly suitable, are, for electro-osmotic purposes, almost without exception electro-negative, so that the process is favorably influenced by the addition of a small quantity of ammonia, caustic soda, etc. The displacing liquid is introduced and the displaced liquid removed at places corresponding to the specific gravities of the respective liquids. For example, the displaced fluid is drawn off at the lowest point if its specific gravity is greater, and at the highest point if its specific gravity is lower, than that of the displacing fluid. The displacing fluid is cooled before use, enabling stronger currents to be employed without the risk of attaining dangerous temperatures.

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[1] G. Gentieu, U. S. P. 931749, 1909; abst. Mon. Sci. 1910, **71**, 136; C. A. 1909, **3**, 2753; J. S. C. I. 1909, **28**, 1065.

[2] D. R. P. 305512, 307701, 307702, 1917; abst. J. S. C. I. 1920, **39**, 74-A.

In the alcoholizing centrifuge as designed by Selwig & Lange and shown in Fig. 237, the basket of the centrifugal has, besides an outer rim, an inner finely perforated one, and a detachable cover of aluminium or bronze for covering the space between the two. In this circular space, which is lined with a cotton sack, the wet gun or collodion cotton (122 lbs. or 60 k.) is rammed somewhat tightly. The detachable cover is then fitted on, and the drum closed with the tightly fitting lid. A finely perforated pipe is then inserted in an opening in the lid, through which the guncotton is given a preliminary coating of weak, already used

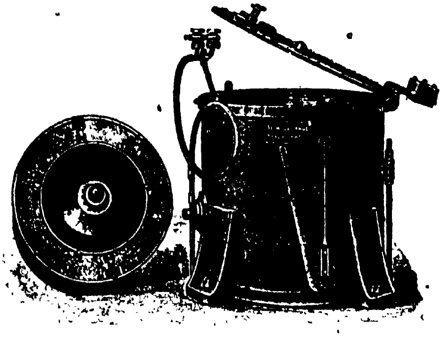

FIG. 237.—SELWIG & LANGE CENTRIFUGAL PYROXYLIN DEHYDRATOR

alcohol, which is followed by a second covering of alcohol of the desired strength. Guncotton treated with alcohol by means of the centrifugal has the same alcohol content (30%-33%) as that which has been hydraulically pressed out.

The output of a centrifugal is said to be about 600 k. of wet guncotton in ten hours, and depending on the diameter of the centrifuge basket.

The drum of the centrifuge has two walls, the inner one with finer perforations than the outer, the space between the two walls being covered with a tightly fitting bronze ring. After removing this cover the perforated surfaces are covered with suitable cotton cloth, the nitrocellulose introduced being firmly packed. The cloth is tucked down over the charge, the ring cover adjusted, and the centrifuge started. At first, rotation should be slow, to permit of even distribution, and also to ensure that the alcohol *displaces* the water, rather than to have the centrifugal force so great that it admixes with it. The maximum speed is given as 1000 r. p. m., and this is continued for 5 minutes.

The alcohol is sprayed against the drum from the inside through a copper pipe having a plurality of fine perforations evenly distributed, the pipe being fed by a rubber hose from the alcohol storage system. At first for the sake of economy, weaker alcohol from a previous operation is used, finally employing fresh alcohol as indicated, according to the nature of the nitrocellulose operated upon, or the final use to which it is intended to be placed.

At first, 35-45 liters of alcohol are sprayed in, and after 12-15 minutes whizzing no further amount of alcohol will run off. Then the strong alcohol is sprayed on to the nitrocotton, until the liquid issuing from the centrifugal has a pre-determined density. The finished nitrocotton is said to contain about 30% alcohol. When operating upon relatively low nitrogen pyroxylins, i. e., the collodions, the strength of alcohol used must, of course, be so adjusted that no gelatinizing effect is induced.

Hydraulic Dehydration. The subject of hydraulic dehydration in general, and solvent hydraulic dehydration in particular, being more correctly speaking a process primarily in conjunction with the manufacture of nitrocellulose smokeless powder, is detailed *in extenso* in Vol. VII of this series under the general heading of the colloidation of nitrocotton into powder grains and granules, and is, therefore, only superficially touched upon here.

Except in connection with the manufacture of guncotton blocks, the hydraulic removal of moisture from nitrocellulose by pressure, unaided by the presence of alcohol or similar body, is seldom attempted. Therefore in speaking of hydraulic dehydration without limiting explanation, it is to be understood as comprehending the use of alcohol as a secondary portion of the process. After the nitrated cellulose has been pulped, poached, and the water removed by centrifugals, the contents of the wringers are either dumped into a waiting car underneath by means of the bottom discharge in the wringer, or to a lead or zinc-lined room underneath the wringer. In either method of procedure, the next operation is to weigh the nitrocotton into batches, one batch per zinc-lined box, the batches being of such size as to just fill the solvent hydraulic dehydrator. These boxes after weighing, and before using for hydraulic dehydration, are usualy stored in a small building adjacent or contiguous to the hydraulic dehydration apparatus, i. e., usually midway between the centrifugal house and the press room. With the proportion of about 30% of water present in the nitrocotton, the boxes and their contents may be stored for long periods with perfect safety before receiving further treatment, the covers used fitting so closely as to be practically air-tight, and admit of but little drying out from escape of moisture.

Instead of centrifugal dehydration, the nitrocotton may be further pulped and blended by passing through a "wet machine" (Fig. 238) from which the pulp issues from the rollers in a flake form, still containing about 30% moisture.

When the nitrocotton is to be "worked up," the contents of one box (in the United States usually 29 lbs. nitrocotton and 11 lbs. of water) are placed in a hydraulic press of type as illustrated in Fig. 251 comprizing a central cylinder to contain the nitrocotton, an upper hydraulic cylinder, and a ram by means of which the central cylinder may be closed on top, and a lower hydraulic cylinder and ram by means of which the nitrocotton in the central cylinder may be compressed.

Both the upper and lower rams are actuated by low pressure water at 250–300 lbs. per square inch, as well as high pressure water at 3000–3500 lbs. per square inch, both being supplied from a central hydraulic pump and accumulator system. The central cylinder is charged with a batch of guncotton as previously described, of moisture content of about 30%, and the top ram is then brought down by low pressure to close the top of the cylinder, after which the lower ram is raised, and the nitrocotton compressed by low pressure. This operation is merely to "block" the material into a compact but porous mass, but little water being extracted upon application of the low pressure.

A prescribed quantity of 92% ethyl alcohol is then pumped through perforations and screens in the upper ram, the latter having been temporarily raised to give space for the entering alcohol, the object being to displace the water, which escapes through the bottom screens and perforations. In some factories, no pressure is at first applied after the introduction of the alcohol, the latter allowed to percolate through the nitrocotton "cheese" by its own gravity and at atmospheric pressure, it being held that by proceeding in this manner, there is a more nearly complete displacement of water by alcohol with a lower miscibility, and hence a smaller amount of weak alcohol to be subsequently rectified is formed.

FIG. 238.—RUNNING PULPED NITROCELLULOSE THROUGH THE "WET MACHINE"

After waiting for a period of from five to eight minutes—depending upon the nature of the nitrocotton—for the alcohol to thoroughly permeate the cheese by gravity alone, high pressure is applied simultaneously to both the upper and lower rams, to press out the excess of alcohol through the screens or perforations in the lower ram. The factors of guncotton porosity and pressure are so adjusted—the latter as to quantity and time—that a known amount of alcohol is left in the block at the close of the high pressure. If for smokeless powder manufacture, the amount of alcohol remaining is adjusted so as to be the proper proportion for colloiding.

After the high pressure is shut off, the top ram is raised by means of the low pressure, and the dehydrated block ("cheese") pressed out by raising the lower ram by the low pressure. Such a block, together with the press that formed it, is shown in Fig. 239.

The weak alcohol pressed out of the nitrocotton is delivered by pipes to the weak alcohol storage tanks at the alcohol rectifying plant. The dehydrated blocks or cheeses are very dense and hard after the high compression to which they have been subjected, and it is necessary to reduce them to a fine powder before incorporation, irrespective of the purpose to which they are to be put, e. g., whether for pyroxylin solutions or smokeless powder. This is usually accomplished in a breaker which consists of an octagonal cage or sieve of coarse wire gauze (shown in Fig. 240) along the inside corners of which are rows of spikes. The cage revolves at about 30 r. p. m. The blocks are roughly broken by hand, either in a hopper leading through one end of the case in which the nitrocotton is further broken up until fine enough to pass through the meshes of the gauze, or else the blocks are broken up by means of a wooden mallet, bone knives or copper or lead hammer. The finely disintegrated and fluffy material is shown in Fig. 241.

In the method of dehydration by pressure as evolved by J. France,[1] and intended primarily for pyroxylin thermoplastics, the wet mass of nitrocellulose is placed on cloth in several superimposed layers, and the whole submitted to strong pressure. In order to further remove water which has not been eliminated by pressure, alcohol is now forced through, followed by air to remove

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[1] U. S. P. 420445, 420446, 1890; abst. J. A. C. S. 1890, **12**, 22. D. R. P. 50921; abst. Chem. Tech. Rep. 1890, **29**, I, 113; Ind. Bl. 1890, 294; Ber. 1890, **23**, 475; Chem. Centr. 1890, **61**, II, 31; Tech. Chem. Jahr. 1890, **13**, 154; Wag. Jahr. 1890, **36**, 1178.

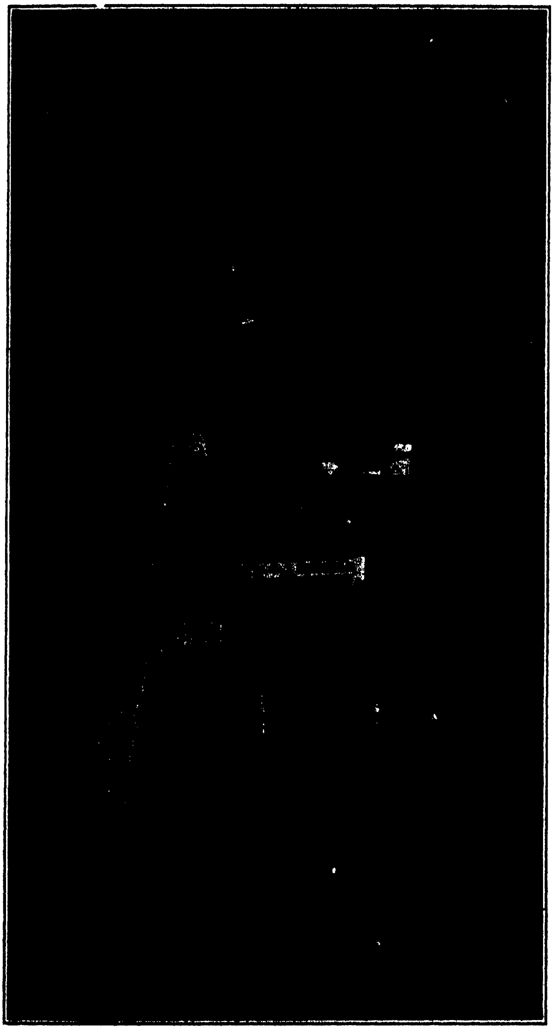

FIG. 239.—DEHYDRATING HOUSE SHOWING PRESSES AND CAR LOADING PLATFORM, ALSO CHEESE BEING WEIGHED

the alcohol, for which purpose the press is especially equipped. The pressing case is so arranged that it can be dismantled, and is provided with a head piece, with a strong sieve and a tail piece, and further with a receiver which has a false bottom. Air and alcohol enter through the sieve at the head, and flow through the false bottom.

It was in 1897 that F. du Pont obtained patent[1] protection for a method of "ridding" nitrocellulose of water by pressure and alcohol, and in this patent he undoubtedly laid the foundation for the modern art as we now know it. His apparatus, shown in Fig. 242, is a pertinent example of progress in this direction, when compared with the ponderous presses shown in the preceding illustrations. Inasmuch as this process may be regarded as embodying the basic ideas of modern practice in this direction, the underlying principles of his method will be mentioned somewhat in detail.

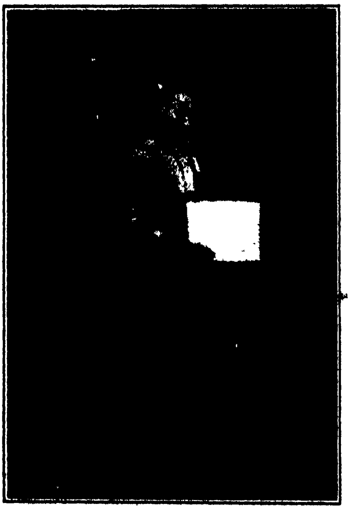

FIG. 240.—A BLOCK OR "CHEESE" OF NITROCOTTON AS TAKEN FROM THE HYDRAULIC DEHYDRATION PRESS

The object of the process of treating guncotton which is described in this patent, is to free guncotton from water without the use of a drying process. The general plan adopted is to draw off the water by suction, and to feed sufficient alcohol at the other end to complete the driving-off of the water, the material then being in a condition ready for the application of solvents, the general distribution of alcohol throughout the mass of guncotton materially assisting the flow of the solvent to all parts of the

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[1] U. S. P. 516924, 1894. E. P. 15693, 1897; abst. Arms Expl. 1898, 6, 121.

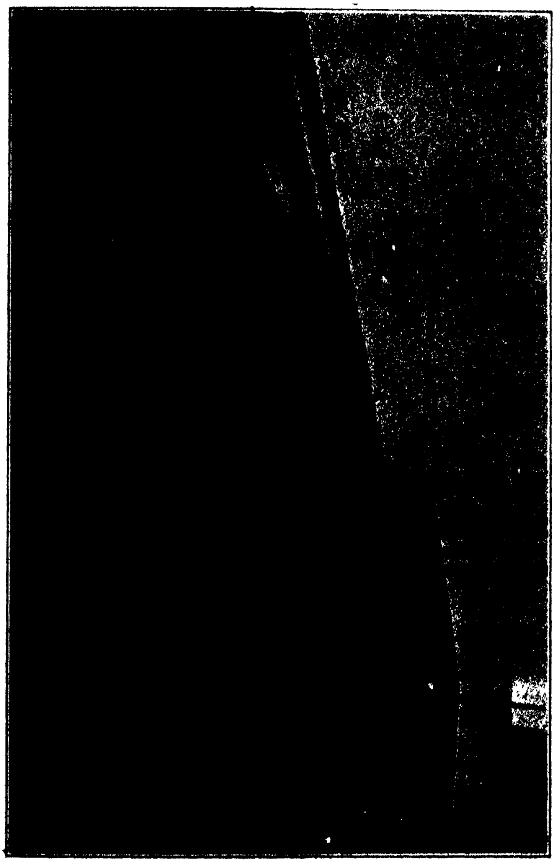

Fig. 241.—Breaker for Disintegrating Blocks of Dehydrated Nitrocotton (Nobel's Explosives Co.)

charge. This process of displacement and substitution has been known for a considerable time in connection with the preparation of other materials than guncotton, the present object being to show how it may be applied to guncotton as a part of smokeless powder manufacture. If wet guncotton is compressed, the water or other non-solvent liquid with which it may be saturated may be carried away as rapidly as it exudes from the guncotton, and the guncotton will be reduced to a state of equal porosity throughout its mass. The water or other non-solvent liquid can then be displaced by the ordinary process of percolation, by a liquid, such as alcohol, which is not a solvent of guncotton. The displacement

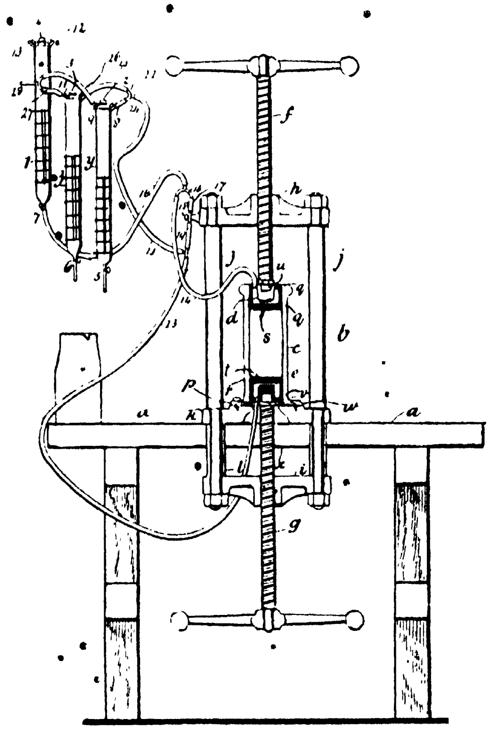

FIG. 242.—DU PONT PRESSURE DEHYDRATOR

will take place irrespective of the miscibility of the liquids, and all of the water or other non-solvent liquid with which the guncotton may at first be saturated will be removed therefrom without appreciable admixture with the liquid which is displacing it. The admixture which does take place is confined entirely to the head of the piston-like column of displacing liquid, so that it can be allowed for in advance, and dilution of the body of displacing liquid following avoided. The exact degree of compression to which the guncotton is subjected in order that percolation may successfully take place may be varied within certain limits without affecting the successful operation of the process, but care must be taken not to compress the guncotton to too great an extent; for a point is reached in the compression of guncotton where the process of displacement cannot be successfully carried on, by reason of the density of the material. Compression must, however, always be exerted in order to bring the material to a condition of equal porosity, and this compression will be in excess of that which can be effected by the weight of the atmosphere alone, when air is withdrawn from the chamber.

The apparatus which has been devized in order to carry out this process, in so far as it relates to the displacement of liquids in guncotton, is shown in the accompanying drawing (Fig. 242), which is an elevation, partly in section, of the press.

To produce the desired compression of the guncotton to be treated, a press constructed so as to permit air to be withdrawn from the compression chamber is used. The compression can thus be effected in two easy stages: first that due to the pressure of the atmosphere as the air is gradually withdrawn from the compression chamber; and second, that due to the additional pressure occasioned by the manipulation of the press. The liquid which is forced from the guncotton during the compression is collected in glass vessels, which are arranged beside the press, and which are finely graduated, so as to enable the operation of the process to be followed with exactness.

In the illustration *a* shows a table which forms a base or support for the press *b*. The press *b* consists of a cylinder, *c*, which is provided with two head blocks or ends, *d* and, *e*, both of which are regulated in position by the action of the screws *f* and *g*, respectively. These screws work through bearing plates *h* and *i*, which are supported and held in position by the brackets *j*. In the construction shown, the brackets *j* extend downward through the base-plate *k*, to which the cylinder *c* is directly bolted, and through the table; and have attached thereto the lower bearing plate *i*, as well as the upper bearing plate *h*. The brackets *j* are shouldered at the point where they pass through the base-plate *k*, and collars *l* are placed around the portions of the brackets between the lower plate *i* and the base-plate *k*. The chief feature, however, consists in the pressure blocks *d* and *e*, which fit air-tight within the cylinder of the press. The interior of these blocks is hollowed out to form chambers *m* and *n*, which are in connection with the outside of the press, through openings *o* and *p* formed on the outer face of the same, and are in connection with the interior of the press by a series of perforations *q* and *r* formed on their inner faces. Over the inner face of the blocks a wire cloth of fine mesh *s* and *t* is stretched, the purpose of which will be explained below. It is intended that the pressure block *d* may be removed from the press, and, when removed, be entirely separate from the screw *f*, so that the only connection between the two is a recessed portion *u* in the outer face of the block within which the end of the screw *f* plays. The lower pressure *e* is, however, not to be removed from the press, and as it is to be moved in both directions by the screw *g*, it is connected to it by the ring *v*. In order to insure the pressure block *e* resting tightly against the lower end of the cylinder when drawn down to its lowest limit, a strip of packing *w* is used, which is placed upon the inner flange *x*, the latter serving to limit the downward movement of the pressure block *e*.

The glass measuring vessels which are used in connection with the press for collecting the liquid which is expelled from the mass of guncotton are shown at *y* and *z*. In the glass vessel *1* is contained the alcohol which is to displace the water in the guncotton, when the latter has been sufficiently compressed to enable the process of percolation to be successfully carried out. All of the glass vessels are finely graduated, so that their contents can be determined with exactness at any time. The various stages of the process can thus be followed, and the extent to which they are carried noted by reference to the volume of liquids in the various vessels. Each vessel is provided with an opening in its top through which it may be filled, and is closed by corks *2*, *3* and *4*, respectively. The discharge openings are closed by cocks *5*, *6* and *7*, respectively; and two openings in its upper end enclosed by cocks *8* and *9*, *10* and *11*, *12* and *13*, respectively.

The connections between the glass vessels and the cylinder of the press are as follows: From the opening *o* in the upper pressure block *d* leads a tube, *14*, which extends to the glass connection *15*. From the glass connection *15* extends a tube, *16*, leading to the discharge outlet of the glass vessel *1*, and the short tube *17*, which leads to the cock *18*. From the other end of the cock *18* extends a tube, *19*, which leads to the glass connection *20*, from which extends a tube, *21*, leading to the glass connection *22*, and the tube *23* leading to the opening *p* in the lower pressure block *e*. From the glass connection *22* extend two tubes, *24* and *25*, respectively, which lead to the cocks *8* and *9*, respectively, of the measuring vessels *y* and *z*. From the cocks *9* and *10*, respectively, of the measuring vessels *y* and *z*, extend tubes *26* and *27*, which lead to a common glass connection *28*. The glass connection *28* is connected to an air pump, which is not shown in the drawing.

If the connections be traced, it will be seen that by proper adjustment of the cocks, air can be withdrawn from one or both ends of the cylinder chamber, and the liquid expelled from the guncotton may be collected within either of the measuring vessels *y* and *z*. It will also be seen that the measuring vessel *1* can be connected with the upper pressure block *d* at the same time that liquid is being withdrawn through the lower pressure block *e*.

In working the apparatus the pressure block *d* is removed from the press, and the pressure block *e* lowered to its extreme limit, so that the compression chamber is ready to receive the mixture of guncotton and water, which is then poured in. In the treatment of guncotton for the manufacture of smokeless powder, the amount of alcohol to be introduced into a given weight of guncotton is fixed and determined by the character of the explosive which it is desired to produce. It is convenient, therefore, to know the exact amount of guncotton contained in the mixture placed within the cylinder of the press, so that the mixture is best drawn from a large vessel in which a known quantity of guncotton is held suspended in water by the action of a mechanical agitator, so that any specimen of liquid withdrawn will represent the entire mixture, and will contain a weight of guncotton determined by the amount of mixture withdrawn. The cocks *18*, *10*, *11*, *5*, *6* and *7* are then closed, and the vacuum pump connected with the glass connection *28* is put into operation. The water contained in the mixture of guncotton will be withdrawn by the suction resulting from the action of the vacuum pump, and will be collected within the measuring vessel *y*. When the withdrawal of liquid in this manner has been carried as far as is practicable, the pressure block *d* is lowered into the cylinder and the cock *a* opened, so that a vacuum will be applied at both ends of the cylinder of the press. Should the measuring vessel *y* become filled with liquid the cocks *8* and *9* may be closed, and the cocks *10* and *11* opened, so that the liquid discharged will be collected within the measuring vessel *z*. The measuring vessel *y* may then be emptied by withdrawing the cork *2* and opening the cock *5*, in readiness to have the flow of liquid diverted into it in a later stage of the process. When the compression produced by the vacuum has been carried as far as is practicable, the screw *f* may be lowered, and the pressure block *d* forced downwards, until the guncotton is compressed to a sufficient degree to permit the process of percolation to be satisfactorily carried out.

The alcohol which is to displace the water in the guncotton is contained within the glass vessel *1*. As a convenient means for enabling the operation of the process to be watched with greater certainty than would otherwise be the case, it is found convenient to color the alcohol, for which purpose the dye called "cudbear" is suitable. The air-pump still working the cock *18* is closed, and the cock *7* opened. The conditions are now such that the colored alcohol contained in the vessel *1* passes down the tube leading from the lower cock of *1*, and finds its way to the interior of the block *d*, and from thence by the perforations in the block and the wire gauze before mentioned, to the cake of guncotton contained in the cylinder. A very perfect displacement now occurs, the water being drawn off by the vacuum applied, and collecting in the vessel *y*, the cocks *10* and *11* being closed, and the cocks *8* and *9* opened for this purpose. The water flows uninterruptedly into the vessel *y*, until it has been entirely removed from the cake of guncotton, when the color of the alcohol appears in the glass connection *20* below the cock *18*. This alcohol will be in a diluted condition, both because of the water contained in the tube *23*, and because, in the displacement of water in the mass of guncotton by alcohol, the line of demarcation between the alcohol and the water, as the former passes down through the cake, while sharp and well defined, is frequently not perfectly horizontal. This causes the alcohol to go out on one side of the bottom of the cake a little in advance of the other, thus causing greater admixture than would otherwise occur. When the color of the alcohol appears at the connection *20* of the tubes, the cocks are changed. *8* and *6* are closed and *10* and *11* opened, thus allowing for the collection of the weak alcohol in the vessel *z*, which has previously been emptied of its contents. When a small amount of the weak alcohol is collected in the vessel *z*, the color of the liquid in the glass connections will be found to have deepened, and the appearance will be that of the original colored alcohol contained in *1*. When matters have progressed thus far the cocks are again changed. *10* and *11* are closed while *8* and *9* are opened—the vessel *y* having been emptied of its contents in preparation for this operation. The supply of alcohol from the glass vessel *1* is now shut off by means of the cock *7*, the cock *18* is opened, and pressure is applied by means of the upper screw *f*. The vacuum is now applied to the upper and lower blocks of the press simultaneously, and the alcohol that is squeezed out by the pressure is collected in the measuring vessel *y*. The compression upon the cake of guncotton in the press is now only limited by the amount of the alcohol which it is desired to leave in the cake. The alcohol which is expelled will be found to be of the same strength as the original alcohol contained in the vessel *1*, and, having not been injured in the process, may be used again for another pressing.

Solvent Hydraulic Dehydration. The question of relative efficiency of centrifugal dehydration as compared with hydraulic dehydration, both being with a nitrocellulose non-solvent, is dependent in a great measure upon whether fibrous or pulped nitrocellulose is being operated upon. Hydraulic is undoubtedly preferable for pulped nitrocellulose. Certainly from the point of output in a given time, the centrifugal method is much the superior. The efficiency of either displacement method is in a large measure also dependent upon whether the water is to be displaced by a nitrocellulose non-solvent not miscible with water, such as fusel oil, or with one which like alcohol is freely miscible with water in any proportions. The author holds to the opinion that a nitrocellulose non-solvent is preferable in that it apparently shoves the water out before it instead of mixing with it and therefore a smaller amount of dehydrating fluid is required to remove the moisture from the given weight of nitrated cellulose. When the two processes are worked upon the same pulped nitrocellulose about three hours are required for hydraulic dehydration and 45 minutes for centrifugal dehydration; a 45 pound charge being operated in the hydraulic press whereas 100 pounds of the finished product can be obtained from a centrifuge in the same length of time, both calculated on dry cellulose weight.

Solvent Displacement without Pressure. F. Nathan and J. and W. Thomson[1] have disclosed a process for solvent displacement in nitrocotton which does not involve lateral (centrifugal) or downward (hydraulic) pressure. The invention relates to the removal from nitrocellulose of the water left after washing, by replacing the water by alcohol to avoid the necessity of drying. The object of the invention is the replacement of water by alcohol without the use of pressure, and in such a manner that a very small amount of dilution of alcohol with water takes place.

The nitrocellulose in the condition in which it is left after purifying, is covered with water so that practically all air is excluded, after which alcohol is slowly and quietly run on to the surface, so as to form a layer of alcohol and a sharp line of demarcation between the latter and water. This is accomplished by allowing the alcohol to flow gently down the sides of the vessel. A cock or valve at the bottom of the vessel is then partially opened, so that the water is allowed to flow away at the rate of one-half to one inch per hour. As the level of the water falls, the alcohol follows it and replaces it in the interstices of the nitrocellulose, fresh alcohol being added at the top of the vessel as required.

This treatment is continued until all the water has been displaced by alcohol, as shown by the sp. gr. of the effluent falling until it is the same as the alcohol. It is claimed that there is very little admixture of the alcohol with the water, so that a relatively small amount of alcohol is required to be rectified. After the dehydration of the nitrocellulose has been completed in this manner, as much as possible of the alcohol is removed by draining, and then centrifugalized. As will be noted, the essential feature of this process is the omission of all pressing, and, in contrast to the operations previously described herein, involves the actual immersion of the material to be treated in water so as to obtain at the start a definite surface of separation between the alcohol and water. The vessel used, if cylindrical, should be of diameter equal to or greater than its depth.

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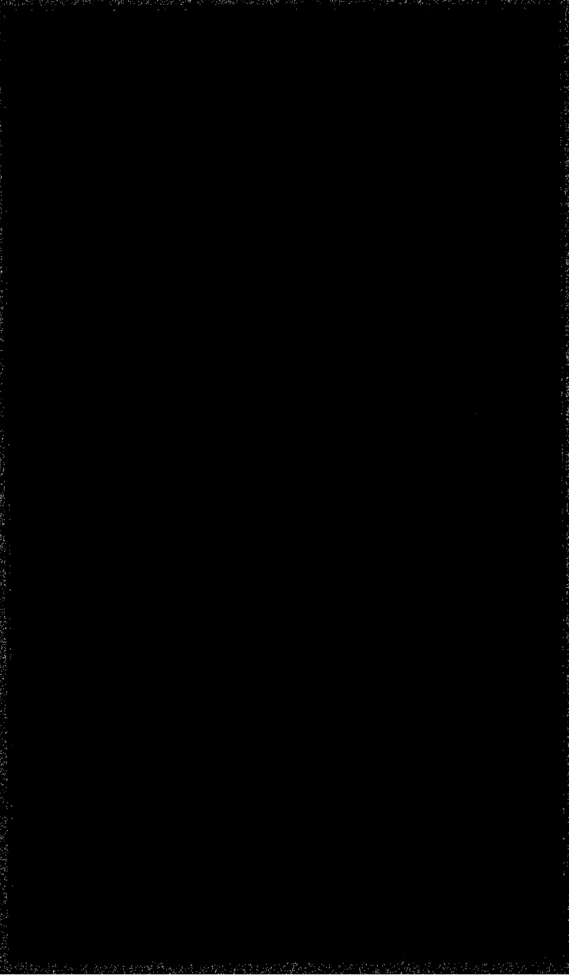
[1] E. P. 7269, 1903; abst. J. S. C. I. 1904, **24**, 385; Chem. Ztg. Rep. 1904, **28**, 732; Arms Expl. 1904, **12**, 54.

In the method of Blair, Campbell and McLean, shown in Figs. 243 and 244, the plant consists essentially of large steel cylinders into which the disintegrated wet nitrocotton is packed. Each cylinder holds the equivalent of about 300 lbs. of dry nitrocotton. Alcohol of 92% is passed through the material by means of compressed air until the sp. gr. of the alcohol issuing from the bottom of the cylinder is substantially the same as that at the top. No liquid issues from the bottom of the cylinder for the first 8 minutes of the dehydration process, after which water only issues until about 15 minutes have elapsed, when the gravity begins to drop to 0.998. From this point the liquor following is treated as weak alcohol, and is diverted to the storage tank.

It requires about 25 minutes to thus dehydrate the nitrocotton, the total amount of alcohol added being 100 gallons. About half of this quantity is obtained from the space above the nitrocotton, and being still strong alcohol, is run off to a storage tank for re-use. For each 100 lbs. of dry nitrocotton thus dehydrated, 50 lbs. of 75% alcohol by weight are obtained.

The dehydrated nitrocotton is removed from the cylinder by means of compressed air, and after being broken up is transferred to large centrifugals in which it is wrung until the alcohol content is reduced to about 30%.

In a recent process of R. Müller a rotary suction machine is combined with a device for the counter-current washing of the material with alcohol of progressively increasing strengths. A pulp containing not over 10% of nitrocellulose, can be treated in this manner, according to the assertion of the patentee.



[illegible]

The process as patented by G. Gentieu,[1] Fig. 245, claims to provide a rapid and inexpensive process for dehydrating which does not cake the material treated or injure the cellular structure of the same. The cellulose is first introduced into a high speed centrifugal wringer to remove the major portion of the water and to matt the nitrocellulose against the perforated wall of the wringer, after which alcohol or other suitable liquid is sprayed against the inner surface of the mass of nitrocellulose while the wringer continues to revolve; the solvent therefore forces its way through the pulped material, thereby displacing the water and leaving in the finished product the required amount of alcohol. The patentee in this manner endeavors to eliminate the expensive hydraulic press and accessory parts and to obtain material which is not compressed into a hard, compact mass, but retains practically its original light and porous condition throughout the process.

The pyroxylin plastic manufacturers dehydrate nitrocellulose by first wringing in a centrifugal, then placing in an air-tight iron can about 28″ × 36″ which holds from 30 to 35 pounds of pyroxylin. Thirty gallons of alcohol are placed in this can and the pyroxylin allowed to cool at ordinary temperatures for about four hours, after which the contents of the can are placed in a centrifugal. In this manner the moisture is reduced to less than 3%.

E. Berl and M. Delpy[2] have conducted an investigation of the material extracted from cellulose nitrates in the course of manufacture by the alcohol used in removing the water from the pulped material. The alcohol is rectified and used repeatedly, the dissolved material accumulating in the still. This residue when dried, has been found to be a brown powder contaminated with oxide of iron and salts of calcium and sodium from the wash waters. When purified by dissolving in ethyl alcohol and precipitating in water, it is a brown powder with an ignition temperature of 102°. About $^2/_3$ of this material will dissolve in ethyl alcohol or ethyl ether, evaporation of the latter leaving a yellowish powder. Anhydrous ether, however, fails to dissolve it. The molecular weight has been determined as 1188, ignition temperature 174° and nitrogen from 9.88% to 10.06%. The portion insoluble in ethyl alcohol is a violet colored powder containing 7.45% N and detonating at 157°. Stabilized nitrocellulose from the same factory had an ignition temperature of 181.5°. These authors point out the fact that the real stability of

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[1] U. S. P. 931749, 1909; abst. C. A. 1909, **3**, 2753; J. S. C. I. 1909, **28**, 1065; Chem. Ztg. Rep. 1909, **33**, 597.

[2] Z. Schiess. Spreng. 1913, **8**, 129; abst. J. S. C. I. 1913, **32**, 452; C. A. 1913, **7**, 2307; J. C. S. 1913, **104**, i, 1305; Chem. Zentr. 1913, **84**, II, 493; Meyer Jahr. Chem. 1913, **23**, 363; Wag. Jahr. 1913, **59**, I, 457; Zts. ang. Chem. 1913, **26**, II, 447. For the physics of the application of centrifugal force to suspensions and emulsions, see E. Ayers, Met. Chem. Eng. 1916, **14**, 500; abst. C. A. 1916, **10**, 1915; J. S. C. I. 1916, **35**, 676; Ann. Rep. Soc. Chem. Ind. 1916, **1**, 188; Chem. Zentr. 1916, **87**, II, 866.

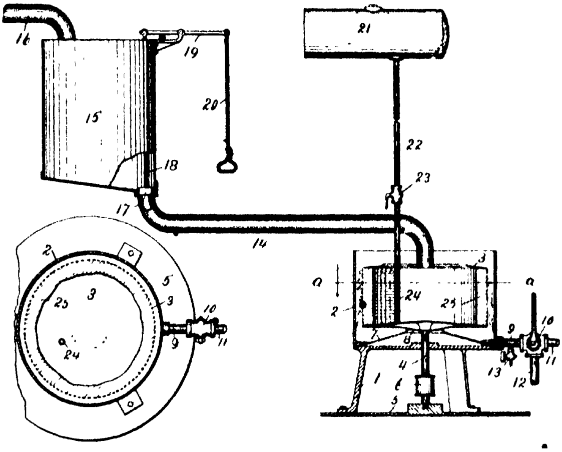

FIG 245.—GENTIEU GUNCOTTON DEHYDRATOR

nitrocellulose cannot be accurately judged by means of the ignition temperature and this was shown by tests on mixtures of purified nitrocellulose with 10% to 20% of these unstable products. The ignition temperature of the mixtures was about 180°. The alcohol-soluble products are considered as part of those nitric esters of disintegrated cellulose material the removal of which constitutes an additional purification of the nitrocellulose. The viscosity of the unstable material in 2% acetone solution was but little greater than that of the pure acetone.

Drying Nitrocellulose. The nitrated cellulose as it comes from the centrifugals carries from 25%–35% of moisture, depending upon the speed of the wringer and the time in which the nitrocellulose is subjected to centrifugal action. The physical condition of the nitrocotton has also an important bearing upon the speed of removal of moisture, while the number and diameter of the perforations in the wringer basket also materially affect the speed of dehydration.

Either the nitrocotton in this condition is placed in tin or zinc lined boxes and stored until it is to be used—the moisture content meanwhile being periodically determined—or else the solvent is removed either by displacement hydraulically with a fluid miscible with water, but substantially a non-solvent of the nitrocellulose, in which case the nitrocotton is intended for immediate use, or else the remainder of the moisture is removed by exposure to the atmosphere, either at normal or reduced pressure. Various modifications of the two above mentioned fundamental methods have been proposed, the more meritorious of which are detailed below.

1. *Removal of Moisture from Nitrocellulose at Normal Pressure.* A nitrocellulose dry plant of this description usually comprizes a frame or corrugated iron building, the roof of which is so connected to the sides of the building that it is easily removable, as by the force of an explosion, and with an efficient system of ventilation. The floor should preferably be of poured concrete to avoid cracks or holes into which guncotton dust may accumulate, this floor being covered with either a lead flooring or a second floor composed of rubber. Lead floors have given excellent satisfaction, the seams being burned, and the lead being carried up at least a foot around the sides, forming a baseboard. The sides of the building are preferably plastered, the racks upon which the frames containing nitrocellulose are spread, being efficiently grounded to minimize the danger of sparking.

The frames are of wood, covered with cheesecloth tacked to the frame by copper nails, each frame holding from 5 to 10 lbs. dry nitrocellulose, the latter being spread by hand on the frame to a depth of two to three inches. Warm air at a temperature not exceeding 40° is circulated through the drying chamber, the air having been previously dried and heated by passing over steam coils. The uniformity of the heat in the dry house has much to do with the stability, which decreases with increase of temperature and of moisture, although the atmosphere has an effect.

The Société anon. de Droogenbosch[1] seek to overcome some of the difficulties of drying nitrocellulose in this manner by introducing ammonia vapor with the warm air, whereby the excess of moisture is removed, the nitrocotton at the same time acquiring a slightly alkaline reaction, considered by the patentees to be distinctly beneficial.

The question of dust—finely divided particles of nitrocellulose—is of great moment in the drying of guncotton, the fibrous nitrocotton being more readily deprived of moisture than when in the pulped condition, unless especial care is taken with the latter to ensure that it is uniformly spread on the trays in thin layers. Where the material has previously been moulded into blocks (see p. 2160) by hydraulic pressure, the minimum of dust is liberated.

There appears to be a wide variation in opinion as to the maximum temperature at which it is discreet to maintain the drying chambers (stoves) some writers contending that temperatures as high as 65° may be maintained indefinitely with impunity, but the consensus of conservative opinion would indicate that prudence forbids temperatures much above 40° inside the drying chamber being kept for any considerable length of time, and that it is preferable practice to dry for a longer period at a less elevated, but uniform temperature.

The warm air should preferably enter the dry house at or near the ceiling, and be withdrawn from near the floor, the outlet having at least an area 25% greater than the inlet. While the entering air may be from a single point, the outlet should be several in number and distributed throughout the chamber.

The reason for blowing the warm air in at the top of the drying chamber and withdrawing from near the floor, is that as the air becomes heavier from absorption of water vapor there is a tendency to sink, although the water vapor itself is lighter than the air. The explanation of this apparent inconsistency is that the cooling produced by the conversion of water into vapor is so great that the air after absorption of moisture is materially denser. It follows, therefore, that if the dry air is admitted at or near the bottom, the fresh and dry air tends to at once rise to the top and escape from the outlets before it has fulfilled its function of absorption with maximum efficiency.

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[1] E. P. 5076, 1901; abst. Mon. Sci. 1905, **63**, 322; J. S. C. I. 1902, **21**, 546. According to Guttmann, this process is objectionable because the nitrocotton is thereby completely insulated, and there is danger of an electric charge, especially with elevated temperatures. To obviate this apparent danger he suggests that copper plates be provided for drying, having conical apertures of $^1/_4$ mm. diameter on top and 1 mm. on the bottom, thus rendering it impossible for them to be clogged by the nitrocotton. To prevent friction the plates may be covered with leather on the edges, and are connected with each other by metallic strips which are carried into the ground. This arrangement renders an accumulation of electricity in the nitrocotton improbable, any electricity developed being carried into the ground.

Great care should be exercised not to subject the nitrocellulose when dry and *warm* to friction or blows, for in this condition it is especially susceptible to sparking from static electricity. The nitrocotton should be allowed to become thoroughly cooled before removal from the drying chamber. The temperature of the dry house should be automatically controlled with temperature registration, and so arranged that a bell is caused to ring when the temperature exceeds the maximum desired. The drying process of the Fabrique de soie artificielle d'Obourg[1] specifies 45° as the maximum.

In the drying apparatus as described by F. Caskey,[2] a vertical cylindrical drying chamber is provided with axial supply and discharge pipes at the top and bottom respectively, and is surrounded by a heating coil, the whole being enclosed in a casing. The pipes at their free ends carry discs, provided with annular channels on their outer faces which engage with corresponding ribs on other discs so as to close the pipes. The lower closure discs carry short tubes sliding within the discharge pipes, and having side openings for discharge, and these discs may be moved axially by a hand-operated screwed rod so as to vary or close the discharge opening. The process of L. Gathmann[3] has more reference to the drying of smokeless powder, although applicable to guncotton and other explosive bodies where there is no solvent recovery required.

In the pyroxylin drying apparatus as perfected by J. Edson,[4] the nitrocellulose is desiccated by means of warm air at not to exceed 38°, which has previously been deprived of its moisture by chilling and passing over lime. As shown in Fig. 246, the

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[1] Belg. P. 188238, 1905.

[2] U. S. P. 1262448, 1918; abst. J. S. C. I. 1918, **37**, 327-A. For drying by electro-osmosis, see Elektro-Osmose A. G., D. R. P. 310681, 1917; abst. J. S. C. I. 1920, **39**, 393-A.

[3] U. S. P. 1289150, 1918; abst. C. A. 1919, **13**, 793; J. S. C. I. 1919, **38**, 200-A.

[4] U. S. P. 249600, 1881. The method of G. Mowbray, U. S. P. 349659, 1886; abst. J. A. C. S. 1886, **8**, 238 in similar.

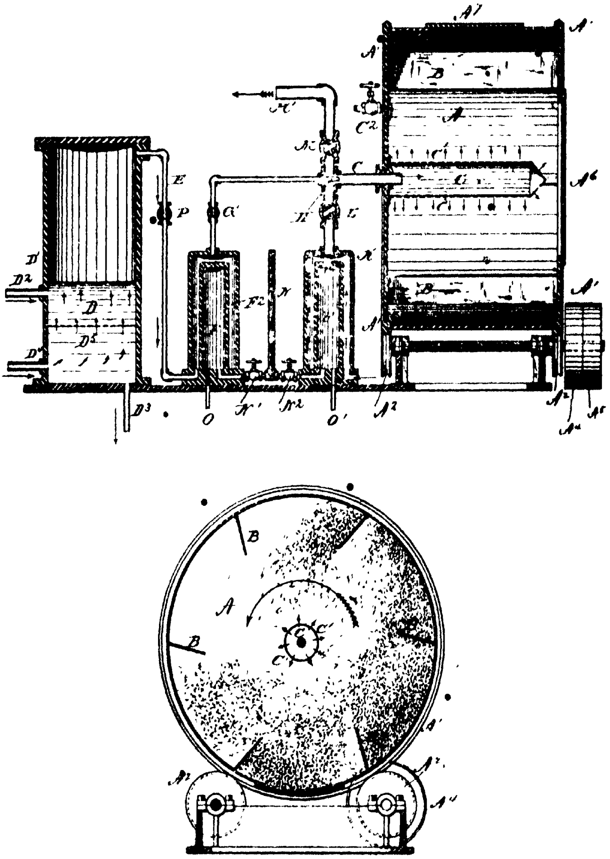

FIG. 246.—J Edson Method of Drying Nitrocellulose

invention consists in the combination of a receiver for holding the nitrocotton to be dried by air cooling and drying apparatus, and an intermediate heater for controlling the temperature of the cold and dry air. The apparatus also, as will be observed from the drawing, comprizes a receiver for holding the material with an agitating apparatus, and air distributing and discharging devices. The pyroxylin is placed in the receiver *A* which is rotatable, provided with openings A^6 and A^7, for the introduction and discharge of the material, the dried air being continually introduced while the nitrocotton is being agitated, thus depriving it of moisture in a minimum of time, and at comparatively low temperatures. It must continually be borne in mind, that dry guncotton being a body which becomes highly electric by slight friction, a strong current of air passing over it might generate sufficient electricity for a spark to leap over and ignite the entire mass.

In those instances where accidents have occurred in guncotton dry houses, and those present have remained alive to tell the tale, the material has often merely burned fiercely without explosive force, i. e., there was rapid combustion, but no explosion. The usual presumption is that the nitrated cellulose has either been subjected to a blow or friction by the workmen, as by upsetting one of the trucks, dropping a frame, or by the friction of sliding a frame in or out of the rack. The workmen, of course, always use rubbers, and the truck wheels are rubber covered.

The danger of drying guncotton may be partially obviated by treating the latter with a small amount of alcoholic or aqueous calcium chloride solution, corresponding to 1%–2% $CaCl_2$ based on the weight of the nitrocotton. The disadvantage of this procedure is the extreme deliquescence of the calcium chloride. In artificial leather manufacture and the production of colored celluloid goods, this amount of calcium chloride would seldom interfere with the value or appearance of the finished product.

In the C. Volney method of drying pyroxylin,[1] the material is placed in a closed vessel, and dry inert gas, or warm air introduced. A certain proportion of the air is then removed from the vessel in order to reduce the pressure, the temperature meanwhile being kept constant between 35°–40°. These processes are alternately repeated, the pressure in the drying vessel fluctuating about 10%. R. Oxland[2] claims that ignition is easier when all

[1] U. S. P. 874265, 1907; abst. C. A. 1907, **1**, 1201; J. S. C. I. 1908, **27**, 92.

Chem. Gaz. 1847, 340; abst. Jahr. Chem. 1847–8, **1**, 1143.

moisture is driven off, and that guncotton will more readily inflame when the moisture content has been reduced under 1%, than when it is 1%-2%.

At the Royal Naval Cordite Factory, Holton Heath, England, after the nitrocellulose has been pulped in the usual manner and run through the centrifugal, it still contains 35%-40% of moisture. It is run directly from the dehydrating centrifugal into a press, where it is formed into a solid cylinder of 14 oz. weight, equivalent to about 9 oz. dry weight. These are placed on copper racks—4500 lbs. per stove (drying building). Air is passed over the cakes at a maximum temperature of 43°, a total drying period of a little over 30 hours being required to bring the moisture content to under 1%.

In the J. Hyatt process[1] for the desiccation of pyroxylin pulp, the material is agitated in contact with bags of porous absorbent material in a closed revolving vessel. The process was designed for the drying of pyroxylin for transformation into celluloid, and is not used at the present time.

The Nobel's Explosives Co. have communicated some data on the subject of drying nitrocellulose in Great Britain with especial reference to their own methods, in which it appears that the nitrocotton is dried by means of hot air which is blown over the material, the latter being either in a loose powdery form as shown in Fig. 247, or when in blocks as illustrated in the photograph shown on p. 2177.

The drying stool consists of a lightly built wooden house surrounded by protecting banks or traverses, and supplied with a current of hot air from a power driven fan situated outside the traverse. The temperature of the hot air is not allowed to exceed 70°. The house is lined with painted canvas, has a lead or linoleum floor, and there must be no exposed iron or other material likely to cause friction.

In the case of loose nitrocellulose shown as illustrated in the photograph, the material is spread on brass gauze trays with wooden rims, and the trays are then placed on wooden frames or shelves. When the nitrocotton is dry, the trays are removed and their contents emptied into canvas bags. The worker when discharging the tray, taps it lightly with his hand to remove any

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[1] U. S. P. 297935, 1884; abst. J. A. C. S. 1884, 6, 207.

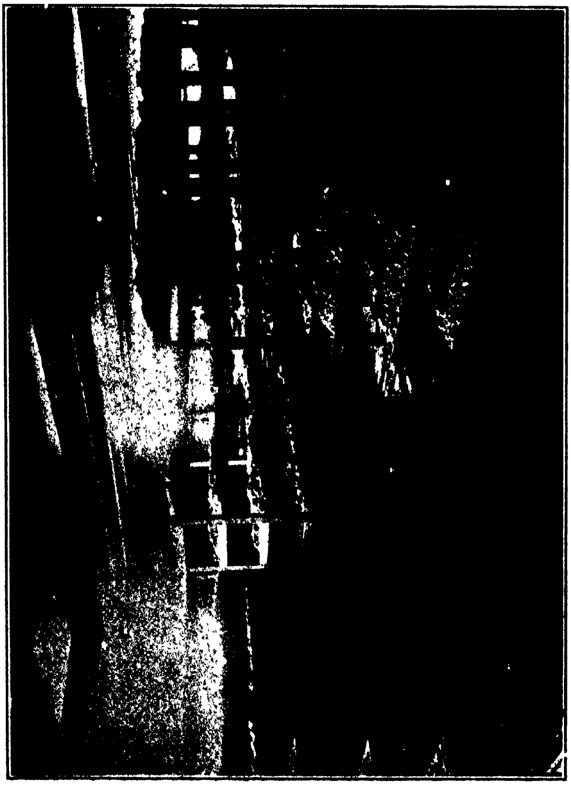

FIG. 247.—STOVE FOR DRYING NITROCOTTON IN LOOSE FORM

nitrocotton still adhering, and as nitrocotton is easily electrified, this has occasionally been noticed to cause sparking. Nevertheless, this method of drying has been used by Nobel's Explosives Co. for many years without accident.

Captain Thomson, Chief Inspector of Explosives, in the course of some experiments found that sparks from an induction coil or Leyden jar would not explode dry nitrocotton blown from a bellows. Great care is exercised to rigidly exclude dirt, grit or other objectionable matter from these houses. The workers wear special pocketless clothing, and remove their boots before entering. A barrier at the door efficiently segregates the interior of the dry house as a "clean area."

In plug or primer drying (see p. 2177) the primers are placed on fixed brass gauze shelves, thus eliminating all movables. In this method there is considerable economy of space and the accumulation of loose dry dust is avoided. In both cases some parts of the stove dry more quickly than others, and a uniform rate of drying is maintained by suitably varying the load.

In Marlow's "Normair" system of drying, which has been proposed, a patent alternator causes the air in the stove to be automatically and intermittently in a state of plenum or pressure and exhaust or rarefaction, thus maintaining in the dry house the air continually alive, and preventing any stagnation or dead centers where there is no movement of air. Hot moist air is also used to utilize the latent heat carrying capacity.

2. *Drying Nitrocellulose under Reduced Pressure.* The advantages to be gained from vacuum drying as compared with drying in a current of air in the usual methods are: (a) greater rapidity of drying; (b) economy of heat; and (c) increased safety.[1] In drying such explosives as nitrocellulose, smokeless powder, mercury fulminate and detonating compositions, vacuum drying insures greater safety because the boiling point of the liquid to be removed is lower at the reduced pressure, and because the effect of the vacuum is to diminish the readiness with which explosions may be initiated and propagated.

It has long been known, for instance, that ordinary gunpowder is ignited imperfectly, if at all, by means of an incandescent wire in highly rarefied air, and under the same conditions guncotton burns very slowly, while even mercury fulminate propagates explosion tardily. Official tests made in the Royal Prussian works at Spandau have demonstrated that large quantities of fulminate could be exploded in a properly constructed vacuum drier, without material damage to the apparatus.

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[1] E. Schweizer, Zts. Schiess. Spreng. 1915, **10**, 38, 53; abst. C. A. 1915, **9**, 1844; Wag. Jahr. 1915, **61**, I, 278.

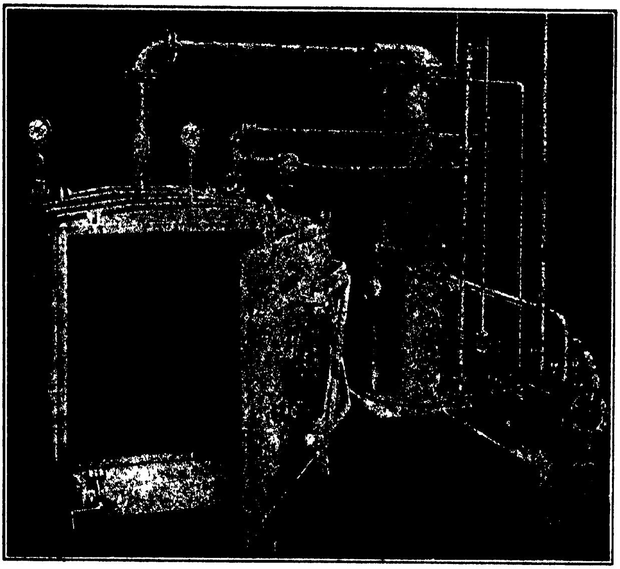

Fig. 248.—Emil Passburg Patent Drying Chamber (J. P. Devine Co., Buffalo, N. Y.)

Of the several types of vacuum driers which have been designed for the drying of such explosives as nitrocellulose, the E. Passburg system of drying chambers as built by the J. P. Devine Co., Buffalo, N. Y. has proven satisfactory.[1] The apparatus, as shown in Figs. 248 and 249, consists of a cast-iron or wrought-iron chamber or cylinder, hermetically closed at one or both ends by large doors. It contains a number of steam- and water-tight heating shelves or pipes, placed one above the other, through which steam or hot water is circulated in order to produce the desired degree of heat, which may be as low as 17°. The material to be desiccated is placed on these shelves in trays of suitable size and shape.

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[1] D. R. P. 28971, 1884; 32252, 1885; 40844, 1887; 56330; abst. Dingl. Poly. 1886, **259**, 86; 1887, **266**, 519, 1888, **269**, 223; 1892, **283**, 102; Jahr. Chem. 1888, **41**, 2614; Eng. 1891, **72**, 447; Sci. Amer. Suppl. 1892, **33**, 13338; Wag. Jahr. 1891, **37**, 439. D. R. P. 125078, 126829, 204381; abst. Wag. Jahr. 1903, **49**, I, 525; 1908, **54**, I, 438.

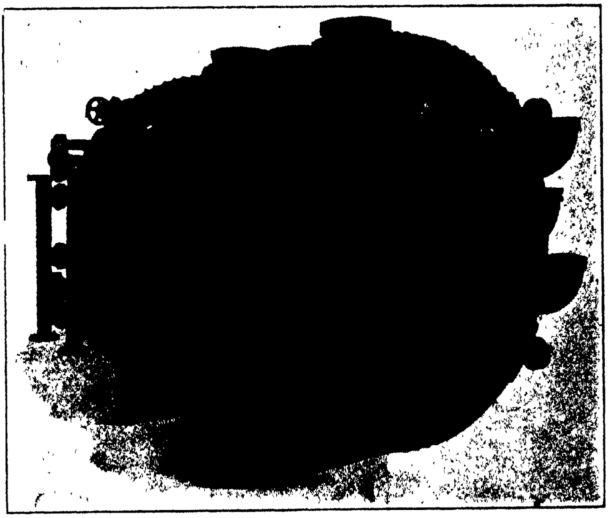

FIG. 249.—PASSBURG SAFETY VACUUM DRYING APPARATUS FOR FULMINATES AND NITROCELLULOSE

The apparatus shown in Fig. 249 is provided with an expansion chamber and other safety devices to receive, in case of explosion, the expanding gases, and thereby decrease their destructiveness. These gases have first to destroy the vacuum in the expansion chamber before they can exercise any pressure on the sides of the apparatus. Any excess pressure then opens the safety valves and apertures to permit the free escape of the gases. In case of extraordinary pressure the whole back of the chamber, which is held in position by springs only, will be forced open, thus affording immediate relief. The chamber is maintained with a vacuum of at least 700 mm.

In drying smokeless powder or other materials where it is desired to regain the solvents contained therein, a large surface condenser is necessary. In drying guncotton which contains water only, a simple injector condenser is used, arranged in such a manner that the vacuum which assists the drying of the material, is created by it.

3. *Drying Nitrocellulose by Miscible Non-solvents.* Of the non-solvents employed in this connection, ethyl alcohol is the most widely used, although the classification of alcohol in this particular as a non-solvent, is, strictly speaking a misnomer, for the alcohol extracts lower nitrated bodies, and in doing so, tends to raise the stability of the nitrocellulose. However, the amount of nitrated cellulose dissolved by alcohol is usually very small, and decreases with increase of nitrogen content in the cellulose nitrated. Alcohol dehydration may be carried out centrifugally or by hydraulic means, as has previously been described.

4. *Drying Nitrocellulose by Immiscible Non-solvents.* In the E. Besemfelder process,[1] the material to be dried is simultaneously or consecutively subjected to the vapors of two or more liquids not miscible with water. A. Cocking and Kynoch, Ltd.,[2] in endeavoring to largely if not entirely overcome the disadvantages and dangers incident to air drying, have described a method of bringing the wet nitrocotton into contact with a suitable liquid or liquefied organic nitrate. Especially suitable in this connection, according to the patentees, is an aqueous emulsion of liquefied trinitrotoluene. The moisture is then removed from the combination by pressure, and the gelatinized nitrocellulose compound used in this condition as an explosive.

In the original process of drying nitrocellulose as evolved by F. du Pont,[3] the wet cellulose ester is placed in a hydrocarbon oil as kerosene, and the oil vaporized, thereby removing the moisture from the fiber. The apparatus which is shown in Fig. 250 consists, of a still especially designed as shown, permitting an automatic return to the still of the oil driven off, while at the same time enabling an accurate determination to be made of the water driven off, on account of its immiscibility with the petroleum hydrocarbon. About 200 gal. of kerosene or benzine boiling at

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[1] E. P. 7975, 1912; abst. J. S. C. I. 1913, **32**, 742; C. A. 1913, **7**, 3203.

[2] E. P. 22311, 1911; abst. J. S. C. I. 1912, **31**, 1095; C. A. 1913, **7**, 1101.

[3] U. S. P. 516924, 1894.

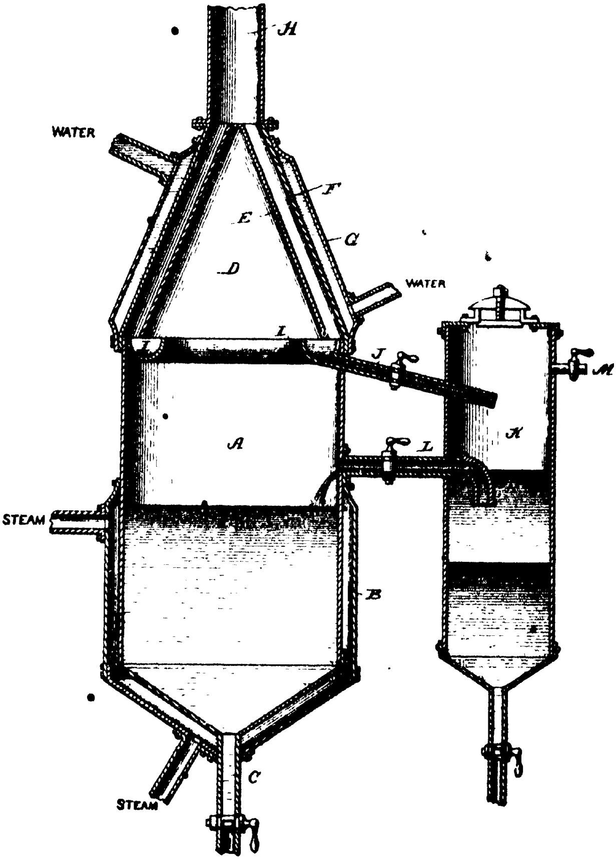

FIG. 250.—F. DuPont Method for Drying Nitrocellulose

about 100° is placed in the still, together with about 200 lbs. pulped nitrocellulose of not to exceed 50% moisture. A vacuum is then placed on the still, steam slowly circulated, and the vapors of oil and water led into a condenser. The boiling point of the oil and the vacuum of the still may be regulated so as to cause the removal of the moisture at a wide range of temperatures.

In a more recent process,[1] a cylinder is arranged within a heating chamber, the upper part of the cylinder being formed of relatively light material so that it will readily rupture in the event of an explosion, a relatively heavy support extending over the cylinder.

An improvement on the foregoing consists[2] in passing the nitrocellulose through a body of heated neutral oil of high flash point, being freed from adhering oil by washing with gasoline. While this latter method was primarily designed for the removal of solvent as acetone from smokeless powder, it is applicable with modification, for the desiccation of pyroxylin.

Quite recently A. Jupeau has contributed to the study of the drying and pulping of nitrocellulose.[3] Drained pulped guncotton contains about 80% of water, which exists as (1) water absorbed in the fiber, (2) adsorbed as a sheath on the fiber, (3) in the interstices of the pulp. This distribution varies with a large number of factors, the principal being the physical and chemical state of the fiber as determined by the origin of the cotton and its previous treatment; the extent of its adsorptive surface which depends on the fineness to which it is pulped; the composition of the liquid; the temperature and the pressure. In an investigation of the effort to be applied in extracting this water it was concluded that (1) for a pulp of given humidity there is a minimum effort to be applied, (2) when the humidity is to be decreased from 75% to 25% this minimum corresponds to a velocity for the centrifuge increasing from 170 to 1000 rotations a minute, (3) a part of a 90% humidity can be removed by simple gravitation, (4) a definite velocity corresponds to a humidity limit. For a velocity of 1000 rotations per minute the humidity limit is 25%. Data and graphs for many observations are given and it is shown that in past practice the work has been delayed because the wringers were overloaded. Thus with a given

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1. U. S. P. 1301409, 1919; abst. C. A. 1919, **13**, 1931; J. S. C. I. 1919, **38**, 480-A.
2. U. S. P. 1232839, 1237551, 1917; F. P. 477343, 1915; abst. C. A. 1917, **11**, 2408, 3438; J. S. C. I. 1916, **35**, 618.
3. Bull. Soc. Encour. Ind. Nat. 1919, **131**, 237; abst. C. A. 1919, **13**, 2127. See also Phot. Jahr. **14**, 97. Neue Erfind. Erfahr. 1893, **20**, 466.

wringer the output was 1920 kg. per 24 hrs., but by reducing the charges in conformity with his curves the output increased to 2300–2500 kg., while the saving in motive force and increase in speed of production was about 25% each. The pulping operation has consumed nearly 50% of the energy used in the manufacture of guncotton. A factory producing 50 tons of guncotton expended more than 25,000 kw.-hr. for pulping alone, corresponding to a daily consumption of 27–28 tons of coal. The fineness to which the guncotton must be pulped is determined by the use to which it is to be put. The accepted method of determining fineness is to place 10 gm. of the pulped guncotton in 250 cc. distilled water in a graduated cylinder, agitate it completely, and allow to settle during a fixed number of hours, when the finer the guncotton the less its volume. By the use of the *finometer* the degree of fineness may be promptly observed as the pulping proceeds in the Horne pulper. The finometer follows the principle enunciated by Stokes. It consists of a 350-gm. sphere of lead suspended by 17 cm. of fine steel wire to which is attached at a distance of 30 cm. from the point of suspension, a horizontal bar graduated in cm. A plumb line hangs alongside this apparatus. The relation between the viscosity of the pulp and the actual fineness of the guncotton is calculated and the corresponding figures on the scale are assigned arbitrary values. The instrument is based on the fact that a sphere immersed in a liquid in motion is acted on according to the degree of viscosity of the liquid. The results from actual practice are remarkable for their uniformity. This investigation demonstrates that the yields depend not only on the charges put in the pulper and the fineness demanded, but also on the proportions of water to guncotton and the contours of the working parts of the machine. The discovery of the relations existing between the 3 factors, charge, water and power, and the yield of pulped material should lead to a considerable improvement in manufacture.

Determining the Yield. In the process of nitration by means of a centrifuge or by displacement, after "drowning" or immersion of the cotton in water from the nitrating bath, the yield may readily be obtained in the following manner. The contents of a certain number of wringers or nitrating units ("dips") is placed in a wooden cart with false bottom, the water allowed to run off and the contents of the cart placed in a laundry centrifugal with 60 to 72 inch basket, where it is rotated while a stream of water is played upon it from the center for a period of 15 to 45 minutes which washes out considerable of the remaining acid. Wringing is continued until no more water is extracted, when the contents of the centrifugal are weighed, a representative sample taken therefrom and the moisture determined.

From this moisture determination and knowing the weight of cotton originally nitrated, the increase in weight or yield is computed. By means of this method it is possible with very little labor, and no loss of time, to determine with accuracy the yield of nitrocotton from one or more units or from the days run. In commercial cotton nitration, this expedient introduced in the process between nitration and preliminary boiling, has been found a valuable check on the efficiency of the nitration processes.

As an example, assuming the contents of five nitrating units of thirty pounds each dry cotton have a gross weight after wringing of 269 pounds and the moisture content is found to be 30%, the increase in yield should, therefore, be 38% on the weight of the dry cotton.

A practical examination of the losses and yield in the practical manufacture of pyrocollodion nitrocellulose is shown in the following figures, taken from an actual and representative run. The gross cotton as received was 50873 lbs., tare allowed 873 lbs., net paid for 50000 lbs.

Losses in wire baling, 256 lbs.; burlap and paper, 910 lbs.; moisture, 2937 lbs.; giving net dry cotton of 46791 lbs. The waste of this cotton was as follows: at the dry house, 37 lbs. (0.074%); at picking house, 56 lbs. (0.112%); in weighing room, 13 lbs. (0.026%); total 106 lbs. (0.212%). In nitration two wringers "fired," and there were 82 lbs. of "scrap." 1580 wringers were dipped, using 230150 lbs. fortifying acid, equivalent to 112359 lbs. HNO_3, 100%. The yield of pyrocollodion per lb. of cotton, 1.45. Yield of finished nitrocellulose powder per pound of cotton, 1.56. Hence 1 lb. finished powder required, 0.64 lb. dry cotton (0.686 lb. cotton as received); 1.54 lb. 100% HNO_3; 3.15 lb. fortifying acid.

Compressed Guncotton. This topic might with propriety, perhaps, have been divided into "Highly Compressed Guncotton

Fig. 251.—Hydraulic Press for Alcohol Dehydration of Nitrocotto

for Torpedoes and Mines," *to distinguish it from a separate but analogous topic on the lower compression of nitrocellulose for* other uses, but as often the line of demarcation between the two subdivisions is not sharply defined, the general subject of guncotton compression is dealt with under the above heading.

In the earlier days of guncotton development when efforts to use it as a propulsive explosive in firearms gave results the opposite of satisfactory, attention was turned towards the employment in solid form for blasting, where the erratic brisance often shown was of lesser moment. As far back as 1866[1] F. Abel patented a process for the solidification, graining and pressing of guncotton into discs, cylinders and sheets, in which solvents were used to combine soluble and insoluble nitrocellulose into a homogeneous and non-friable mass. E. Brown[2] demonstrated that compressed guncotton containing 15%–20% of water retains its explosive properties nearly the same as if dry.

S. Mackie and C. Faure[3] disclosed a method, whereby guncotton in a fibrous state, without being reduced to a powder or pulp, is compressed into cakes or scales by passing it between rollers, or placing it between indented plates and subjecting to hydraulic or other pressure, the sheets so obtained being easily divided along the indentations.

In 1881, J. Anders[4] patented his gelatinous blasting composition, to be moulded into cartridges, in which guncotton is placed in a cylinder contracted towards its lower end, and terminating in a tube of the desired caliber. The explosive is pressed out through the tube by means of a leather covered piston actuated by a screw. The next year disclosed the details of compressed guncotton manufacture as carried out at the factory of Petry & Falkenstein at Düren,[5] the product being "very stable

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[1] U. S. P. 59888, 1866. Ber. 1871, **4**, 883; abst. Deut. Ind. Ztg. 1871, 495; Chem. Tech. Rep. 1871, **10**, II, 219.

[2] Mechan. Mag. 1872, 478; Dingl. Poly. 1872, **206**, 500; 1873, **210**, 393; Poly. Centr. 1873, **39**, 268; Deut. Ind. Ztg. 1873, 38; Wag. Jahr. 1873, **19**, 355; J. C. S. 1873, **26**, 658; Berggeist, Beilage, 1873, No. 96; Poly. Notizbl. 1874, **29**, 63; Chem. Tech. Mitth. 1873–4, **23**, 69.

[3] E. P. 1830, 1873; abst. Chem. News, 1874, **29**, 166; Dingl. Poly. 1874, **213**, 174; Ber. 1874, **7**, 741; Jahr. Chem. 1874, **27**, 1123.

[4] E. P. 800, 801, 1881; abst. J. A. C. S. 1882, **4**, 48; Wag. Jahr. 1881, **27**, 331; Chem. Ind. 1881, **4**, 140, 384; Ber. 1881, **14**, 2318; Jahr. rein Chem. 1881, **9**, 136; Chem. Tech. Rep. 1881, **20**, II, 136.

[5] Wag. Jahr. 1882, **28**, 420. In this connection see Zts. Berg. Hütten u Salinenwesen, 1880, 242; Dingl. Poly. J. 1880, **238**, 330; Berg. Hüttenm.

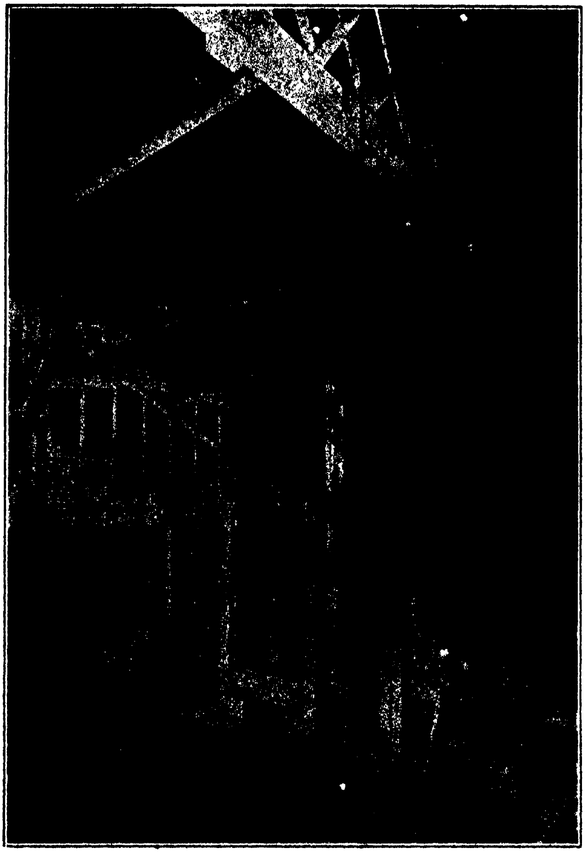

FIG. 252.—HYDRAULIC GUNCOTTON PRESS (FROM BELOW)

against extraneous influences," but the gases liberated upon combustion were said to "be very objectionable." The compressed guncotton of H. Maxim[1] was prepared by incipient solution of the nitrated cellulose in solvents, being made into a cheese by strong pressure, and then hydraulically extruded into forms as desired.

P. Champion and H. Pellet[2] engaged themselves with the subject of compressed guncotton in 1876, but primarily in an academic manner.

In the pamphlet on submarine blasting written in 1886 (Berlin) by M. v. Förster, are detailed experiments with compressed guncotton for the blasting of submerged vessels. In a typical example cited, it required 100 blastings with altogether 1200 kg. guncotton to effectually destroy and remove an iron vessel (tonnage not stated), only the stern being untouched. He describes[3] a process by means of which a charge of guncotton can be kept with its properties unimpaired, under water for a considerable period, while Lauer[4] evolved a method for blasting subaqueous objects with exposed nitrocellulose charges. Following the proposal of F. Abel in 1875 to charge grenades with

Ztg. 1880, 398; Oest. Zts Berg. Hüttenw. 1880, 523; Wag. Jahr. 1880, **26,** 381.

[1] D. R. P. 49154, abst. Chem. Tech. Rep. 1889, **28,** II, 173; Zts. ang. Chem. 1890, **3,** 59; Jahr. Chem. 1890, **43,** 2708; Wag. Jahr. 1889, **35,** 475; Ber. 1890, **23,** 42-C; Industriebl. 1890, 87; Tech. Chem. Jahr. 1889, **12,** 160.

[2] Compt. rend. 1876, **83,** 77, 709; 1877, **84,** 609; abst. Ber. 1877, **10,** 735; Chem. Centr. 1877, **48,** 323, 739; Wag. Jahr 1876, **22,** 479; 1877, **23,** 385; Chem. Tech. Rep. 1876, **15,** I, 388; Jahr. Chem. 1877, **30,** 1159; Jahr. rein Chem. 1877, **5,** 175; see also Mon. Sci. 1876, **18,** 1160; Ber. 1876, **9,** 1610; Chem. News, 1876, **34,** 205; Zts. Chem. Grossgewerbe, 1876, **1,** 233.

[3] Berg. Hütten. Ztg. 1878, 117; abst. Dingl. Poly. 1878, **228,** 284; Zts. Chem. Grossgewerbe, 1878, **3,** 380. Dingl Poly. 1880, **238,** 328. Eng. Mag. 1884, **31,** 113; abst. Proc. U. S. Nav. Inst. 1885, **11,** 109; Chem. News, 1885, **52,** 185. Dingl. Poly. 1884, **251,** 371; abst. Jahr. Chem. 1884, **37,** 1750; Chem. Ind. 1884, **7,** 133; Chem. Ztg. 1884, **8,** 348; Chem. Tech. Rep. 1884, **23,** I, 200; J. C. S. 1884, **46,** 948; J. S. C. I. 1884, **3,** 330. Chem. Ztg. 1886, **10,** 530; abst. Chem. Tech. Rep. 1886, **25,** I, 158. Dingl. Poly. 1886, **261,** 25; abst. Jahr. Chem. 1886, **39,** 2077; J. S. C. I. 1886, **5,** 502; Wag. Jahr. 1886, **32,** 324; Chem. Tech. Rep. 1886, **25,** II, 296; Proc. U. S. Nav. Inst. 1886, **12,** 563. Dingl. Poly. 1888, **269,** 240; Pop. Sci. Mon. 1888, **32,** 133; abst. Proc. U. S. Nav. Inst. 1889, **15,** 373, 513. D. R. P. 22418, 1882; abst. Wag. Jahr. 1883, **29,** 390: Chem. Ind. 1883, **6,** 149, 269; Industriebl. 1883, 279; Chem. Tech. Rep. 1883, **22,** II, 189. M. v. Förster and W. Wolff, D. R. P. 26014; abst. Wag. Jahr. 1884, **30,** 377; Chem. Ind. 1884, **7,** 31, 165; Chem. Tech. Rep. 1884, **23,** I, 201; Bull. Soc. Chim. 1884, **42,** 398; Poly. Notizbl. 1884, **39,** 187. E. P. 3866, 1883; abst. J. S. C. I. 1884, **3,** 378.

[4] D. R. P. 30242; abst. Wag. Jahr. 1885, **31,** 293; Tech. Chem. Jahr. 1884-5, **7,** 158. See also Dingl. Poly. 1885, **64,** 518.

FIG. 253.—COMPRESSION OF GUNCOTTON

water and a little guncotton,[1] M. Förster and W. Wolff in Walsrode advanced the use of guncotton for grenade charges,[2] by superficial treatment with a solvent; for the formation of compressed guncotton blasting projectiles;[3] and for filling hollow projectiles with granulated explosives which were afterwards compressed.[4]

The usual compressed guncotton as previously described had a density of 1.00–1.10.[5] According to W. Rintoul,[6] the average of several determinations of guncotton of 13% N prepared from cotton waste gave 1.675 at 15.5°/15.5° as the absolute density, whereas the figure of 1.634 given in the Service Treatise on Explosives, is therefore somewhat below the truth. When containing not less than 15% of water, compressed guncotton is uninflammable, and may be transported and stored with safety. The specific gravity of guncotton blocks containing no air, but with variable percentages of water is given in the following table:

Water Per cent.	Specific Gravity	Density
18	1 55	1.37
20	1.54	1.34
25	1.51	1 26
30	1.47	1.17

It appears, therefore, that a compressed guncotton of 1.00–1.10 density and containing less than 25% of water, must contain air in the interstices of the material. Another point of importance is, that when making up a mine charge or torpedo head charge from a number of small blocks (see Fig. 254, A), it is obvious that a material amount of space is lost on account of the unavoidable airspaces between the individual segments constituting the finished block. It is apparent, that in a mine or torpedo, the greater the weight of guncotton which can be gotten into the available space, the greater disruptive power will be produced, other factors being equal.

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[1] Nature, **12**, 314; Naturforscher, 1875, No. 40; Poly. Centr. 1875, **41**, 1361; abst. Wag. Jahr. 1876, **22**, 509; Chem. Tech. Rep. 1875, **14**, II, 218; Löbell's Jahr. 1875, 380.

[2] D. R. P. 23808, 26014; abst. Wag. Jahr. 1883, **29**, 389; Chem. Ind. 1883, **16**, 2542; Chem. Tech. Rep. 1883, **22**, II, 188.

[3] D. R. P. 24674; abst. Chem. Tech. Rep. 1884, **23**, I, 204.

[4] D. R. P. 33867

[5] It should be remembered that density refers to the weight of guncotton in unit volume as compared with water, whereas specific gravity refers to the weight of water and guncotton in unit volume of a compressed block.

[6] J. S. C. I. 1907, **26**, 449.

To accomplish this improvement, A. Hollings[1] in 1898 was granted patent protection for a process for compressing large masses of guncotton in such a manner that air is substantially excluded, the compressed guncotton consisting, therefore, of but nitrocellulose and water.

The various patents of Hollings on this subject embrace in their entirety, a means of molding guncotton so that all the air is expelled from the pores of the nitrocotton, the separate fibers being laid together by pressure, thus forming a mass free from air spaces. The invention provides means whereby the guncotton will be prevented from lodging or being caught between the pressing ramhead or disc and the sides of the mould, or if lodged or caught, will be prevented from becoming dry, and thus obviate

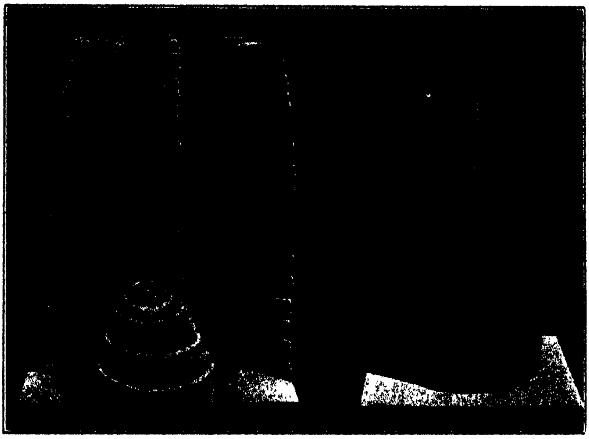

FIG. 254

A.—OLD METHOD, CHARGE OPENED OUT

B.—OLD METHOD, CHARGE ASSEMBLED

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[1] U. S. P. 654398, 660727, 690728; abst. J. S. C. I. 1902, **21**, 276. E. P. 19806, 1898; abst. Mon. Sci. 1910, **72**, 733. E. P. 23449, 1899; abst. Mon. Sci. 1910, **72**, 733. E. P. 3725, 1901. E. P. 8278, 1903; abst. J. S. C. I. 1904, **23**, 560. D. R. P. 124236, 1899; abst. Wag. Jahr. 1901, **47**, I, 494. D. R. P. 125101, 1900; abst. Wag. Jahr. **47**, I, 494. D. R. P. 126974, 1900; Abst. Wag. Jahr. 1903, **49**, I, 365. D. R. P. 129329, 1901. See L. Hale, Arms and Expl. 1905, **13**, 14.

any liability to explosion; also to prevent the guncotton from adhering to the pressing ramhead when the latter is being withdrawn. The methods previously proposed for the formation of segmental blocks containing air spaces therein, are thus obviated by the inventions of Hollings, whose process is sharply distinguished from his predecessors in this field, because the air in the blocks, upon removal of the pressure has a tendency to expand from its normal elasticity, thus rendering the blocks spongy or laminated, diminishing consolidation, and consequently causing faulty or incomplete detonation.

The Hollings processes have been acquired by the New Explosives Co.—to the courtesy of whom much of the information and illustrations in this topic is due—and has been fully descibed in Engineering of May 9, 1902. A completed guncotton block as made by this process is shown in Figs. 255, 256, and the hydraulic press for forming these blocks is illustrated in Fig. 257.

By these processes guncotton blocks have been made of up to 500 lbs. weight, and having a density of 1.25. To produce a single block of this enormous size, the guncotton is mixed with hot water, and the air thereby displaced. The pulp and water is then run into a perforated container 9 ft. long, and this container placed within the press. The pressure to which the guncotton is subjected is $2^3/_4$ tons per sq. in. During the pressing and on the release of the pressure, the guncotton is surrounded with water to prevent the entry of air. The compressed guncotton is then dressed to the desired size by being turned down in a lathe, so that it will exactly fit the mine container or torpedo head for which it was designed. In this manner, the maximum of guncotton can be gotten into a given space. Fig. 263 shows the above described nine feet container in position for filling.

The Hollings process was modified and amplified by G. Bell in a series of patented improvements, the issuance of which began in 1903.[1] The essence of the Bell inventions is that the gun-

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[1] U. S. P. 835296, 835297, 835298. E. P. 17414, 17415, 1903; abst. J. S. C. I. 1904, **23,** 882; Arms Expl. 1904, **12,** 122. E. P. 17890, 1903; abst. J. S. C. I. 1904, **23,** 836; Arms Expl. 1904, **12,** 122. E. P. 10663, 1904; abst. J. S. C. I. 1905, **24,** 690; 1906, **25,** 1175; Arms Expl. 1905, **13,** 90. E. P. 17414, 1904; abst. J. S. C. I. 1904, **23,** 882; Arms Expl. 1904, **12,** 136. F. P. 340373, 340474, 340475, 1904; abst. J. S. C. I. 1904, **23,** 836, 837. D. R. P. 166420, 1904; abst. Wag. Jahr 1905, **51,** I, 450; Zts. ang. Chem. 1906, **19,**

Fig. 255.—Machine for Breaking or Sieving Pulped Nitrocotton (Nobel's Explosives Co.)

cotton pulp is fed into and subjected to pressure in a mold with a perforated end wall adapted to retain the guncotton, and allow the water to pass through. The mold becomes filled with guncotton which is formed into a block. Pistons are provided to compress the block endwise, and the pulp may be fed through the pistons. The mold is provided with means for evenly distributing the guncotton, so as to ensure a uniform density in the finished block. The points of superiority claimed in the inventions of Bell for the manufacture of hydraulically consolidated guncotton blocks are as follows:

1. The nitrocotton is introduced into a chamber exhausted of air, and after the mass has been rendered as free as possible from air, water is introduced into the chamber. The interstices of the block become filled with water, and air spaces are thus avoided.

2. The guncotton press in which the mold containing cylinder is provided with means for making a water tight joint between the ram at the open end. Water under pressure is provided within the casing in contact with and surrounding the charge under compression, so that it shall be available for safety, and for obviating the absorption of air by the charge on its expansion caused by the release of the ram pressure.

3. The invention has for its object to render the density of the block more uniform from end to end than hitherto has been produced, and to produce a given average density with considerable less pressure than heretofore required. To effect this purpose there is employed a stationary receiver adapted to hold the mold containing the charge to be compressed, and two hydraulic plungers adapted to fit within the mold, and to move longitudinally and independently of each other, while acting upon the opposite ends of the block, so as to compress it uniformly between them. Uniform pressure means uniformity of density and of moisture content, it having been found that with the prior methods of guncotton consolidation, each block produced was much denser at the end which had been nearer to the

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152; Zts. Schiess. Spreng. 1906, **1**, 16. D. R. P. 174347, 1904; abst. Wag. Jahr. 1906, **52**, I, 481. D. R. P. 177032, 1904; abst. Wag. Jahr. 1906, **52**, I, 484; Zts. Schiess. Spreng. 1906, **1**, 428. D. R. P. 192588, 1904; abst. Wag. Jahr. 1907, **53**, 426. Ital. P. 72048, 72049, 1907; 73092, 1903. Zts. Schiess. Spreng. 1906, **1**, 234, 235.

ram than at the other end. Uniformity of moisture is essential, it having been demonstrated that if the amount of moisture is too small at any part of the block, the latter will be unsafe, it having been established and usually required by governments that the percentage of moisture shall be *uniformly* distributed throughout the mass.

4. Uniformity of density in the case of a charge of a locomotive-torpedo is absolutely necessary in order that the proper balance of the torpedo containing it be maintained when submerged, for the accurate delivery of such a torpedo depends on very delicate adjustments of weights, poise, and propelling and guiding mechanism, so that a difference in weight between the ends of a torpedo charge might well be sufficient to render the torpedo useless, unless that difference was known beforehand, and the proper allowances made for it in the manufacture. Such adjustments would be difficult and so expensive as to materially interfere with the employment of this type of torpedo.

5. By this method, it is claimed a block of 500 pounds, homogeneous as to density and moisture content, may be formed in from 10 to 15 minutes.

In the method, of the New Explosives Co., Ltd., and J. Carter,[1] the charges are made in longitudinal halves or sections of a size to fit the projectile, etc., by compression in molds, where the pressure is exerted in a direction transverse to the axis of the mold. The sections may then be united by means of collodion solution or the like, to form a single piece, the use of lathe-turning being thus rendered unnecessary. In the apparatus claimed for carrying out this process, the molds for the separate sections are provided with drainage perforations and are open at the upper part to receive the press-head, while mechanical means are provided for bringing them beneath the press-head and removing them after the compression. A movable transverse partition may be fitted into the mold so as to leave a space at the nose. This partition is removed before the compression, so that the pulp may enter the space, with the result that this portion of the charge does not receive pressure in excess of that exerted upon any other portion, relatively, a point of considerable importance.

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[1] E. P. 12378, 1907; abst. C. A. 1909, **3**, 592; J. S. C. I. 1908, **27**, 877. F. P. 380352, 1907. U. S. P. 903840, 1908. Zts. Schiess. Spreng., 1906, **1**, 233; abst. Wag. Jahr. 1906, **52**, I, 492.

The invention of A. Musker[1] has reference to the production of solidified guncotton blocks from the loose or open state, the guncotton being directly introduced into the mold or container in which it is fabricated into blocks in conjunction with a limited amount of water, the latter being supplied in such amounts that the mass remains in a semi-fluid—as distinguished from a freely-flowing or freely-fluid—condition, so that after mixing it can be directly pressed. When the mold has received the charge, it is directly pressed into blocks. The press suitable for carrying out the operation consists of a cylinder having within it the mold vertically disposed, and adapted to swing on a pivot into and out of the swinging position; the ends of the cylinder being covered by end covers which may be hydraulically moved in and out of position. The charge is pressed in the mold by rams at each end. The mixing apparatus is removed from the mold after the mixing, and prior to the pressing.

In comparison to the above modern processes, the earlier methods of C. Du Buit,[2] and of Burkart,[3] are of but historical interest.

In Germany, and also in Austria, the general methods of guncotton block manufacture are stated to be as follows: The nitrocellulose intended for pressing is freed from the excess of water by allowing it to settle in the pulpers and is then suspended in warm water (if possible), and transferred to a vat as a paste, the vat containing a horizontally arranged wheel. Definite amounts of guncotton are either measured off in this tank or weighed out, and first subjected to a preliminary pressing in order to obtain a more compact mass, which will, however, still contain about 50% of water. In order to effect this, the paste or pulp is placed in hollow forms, part of the water removed therefrom by suction, and then pressed mechanically, the pressed mass being then weighed, and the excess (if any) removed mechanically. The guncotton mass is then hydraulically pressed until the specific gravity reaches about 1.20, in which condition from 10% to 20% of water still remains.

The presses used are described by F. Plasch as follows: The pressure cylinder is sunk into the foundation in order to bring the table to a convenient height for working. The supports, of course, are powerfully constructed and mounted to the base usually with four columns. It is advizable to adjust the table for various kinds of guncottons, to insert their respective forms and dies. These latter are strong steel cylinders, provided with a channel in the direction of their longitudinal axis, and of section identical with that of the guncotton bodies to be manufactured.

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[1] E. P. 198, 3725, 1905, abst. J. S. C. I. 1906, **25**, 236.

[2] E. P. 23260, 1894; abst. J. S. C. I. 1895, **14**, 1062.

[3] Dingl. Poly. 1873, **207**, 173; abst. Jahr. Chem. 1873, **26**, 1027.

The height of the cylinders is usually three times that of the bodies of guncotton to be made. A preliminarily pressed piece of guncotton and pieces of steel are next introduced, these steel pieces being of the same size as the hollow of the form, and possess many fine channels running in the direction of the axis, to permit water and air to escape. One to four of these forms are placed inside a heavy iron frame, and fastened.

This iron frame constitutes the main part of the press table, the presses being arranged in such a manner, that in the event of an explosion, the operator will not be injured by flying fragments. Brick walls, wooden casings with a filling of sand, or a heavy rope screen may be used for this purpose, depending upon the locality and type of construction of the press. The valves of the presses are arranged in such a position that the operator can work them from a protected position.

The pressing itself is carried out in the following manner: The lower opening of the form is closed by the die of the press, a preliminarily pressed piece of guncotton and the steel pieces previously referred to being placed in each form, the table adjusted and the inlet valve opened after the operator has protected himself. The piston of the press is raised and the dies enter the form, compressing the guncotton. The valve is closed as soon as the piston has moved up a certain distance, or the full pressure is allowed to remain upon the guncotton for several minutes, especially if unusually dense bodies are desired. One either presses "to measure," or "to time."

In the case of conically shaped bodies where it is necessary to press to a certain definite bulk as well as a predetermined moisture content and density, the manipulation becomes a matter of experience of the operator on an individual machine.

In the United States and England, for instance, the pulped nitrocellulose from the stuff chest is drawn into the molding press, the latter being constructed of bronze, actuated hydraulically, and containing the molds. The pulp is run into these molds, the pressure being applied for about four minutes. The mold-press blocks are then taken to the final press and subjected to a pressure of 6000 to 7000 pounds per square inch through an interval of about three minutes, the maximum pressure being maintained for about one minute.

The blocks as they come from the final press contain from 10%–18% of water, depending upon the pressure to which the charge has been subjected, and the time the maximum pressure was applied. Often while in the press they are stamped with the makers name and the serial lot or date or other distinguishing mark. Such guncotton blocks, slabs or primers before being issued to storage or for service, may be re-soaked in water, until their moisture content reaches about 35%.

In order to prepare guncotton for primers, a block of wet nitrocellulose may be split up into half inch sections, these being strung on copper or brass wire and exposed to a dry atmosphere in diffused daylight. Larger blocks are dried as shown in Fig. 258, the machinery used in their production being illustrated in the photographs shown in Figs. 259, 260 and 261. The sections are periodically weighed, the drying being continued until no further loss in weight takes place. The preceding four photographs are from Nobel's Explosives Co., Ltd., who have made an interesting photographic comparison of cotton and guncotton in different stages of manufacture, as shown in Fig. 262, in which the conversion of 18 lbs. of cotton into 30 lbs. of guncotton is illustrated. Reading from left to right, the seven piles represent, (1), the original cotton as withdrawn from the bale; (2) the same cotton after being teased, willowed, boiled, and prepared for nitration, in which it is observed how the cellulose has increased in bulk incident to the opening-up operations to which it has been subjected in order to increase its receptiveness for the nitrating acids; (3) after nitration and boiling; (4) after pulping and centrifugalizing; (5) after stoving (drying); (6) after molding into primers; and (7) after compression into blocks for despatch.

J. Thomas[1] has observed that moist, pressed guncotton such

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[1] Zts. ang. Chem 1898, **11**, 1003, 1027; 1899, **12**, 55; 1907, **20**, 1143;

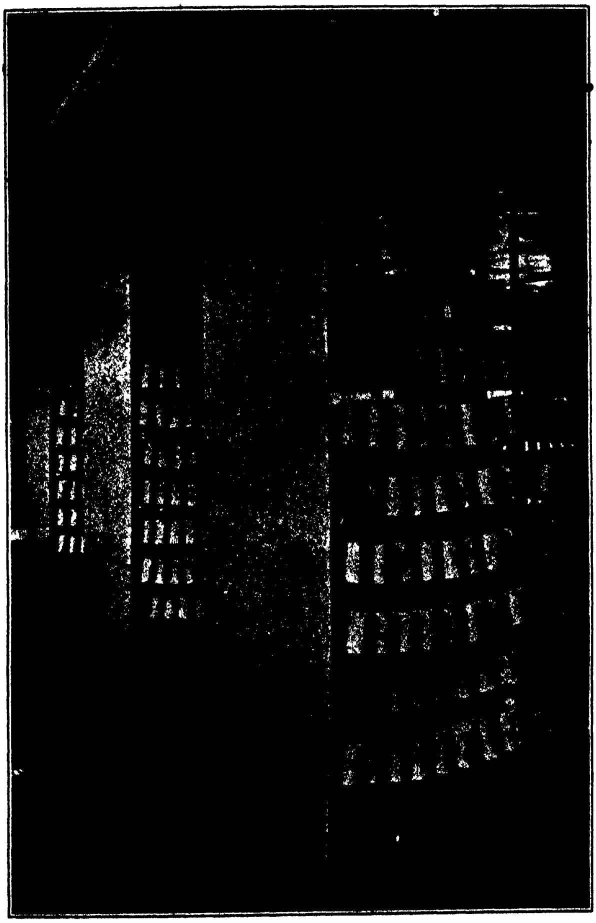

FIG. 258.—STOVE FOR DRYING NITROCOTTON IN PRIMER FORM

[redacted]

as is used for torpedo charges, when extracted with water, calcium nitrite and nitrate can be detected in the filtrate. He explains the presence of these water-soluble calcium salts, by the presence of small amounts of calcium carbonate added by the manufacturers to minimize the development of acidity upon storage, and to prevent the spontaneous decomposition. Thomas is of the opinion that calcium carbonate, even in the small amounts normally introduced in certain approved types of nitrocellulose, induces an appreciable and detectable saponification, partially from the calcium carbonate which is not entirely insoluble in water, and also from $CaHCO_3$, formed by the action of CO_2 normally present in water on the $CaCO_3$. He is not in agreement with O. Guttmann,[1] at least in the case of damp guncotton—that it would be preferable to omit the addition of chalk, for he contends there is always a slight decomposition of such guncotton with the formation of free acid, which if not neutralized by the chalk, forms a nidus for the development of incipient decomposition. In his opinion, however, the neutralization of the free acid more than compensates for the possible deterioration due to the slight saponifying effect of the neutralizant. Often guncotton made for disruptive purposes contains a small amount of sodium carbonate, which, disseminated through the mass of the nitrocotton, tends to neutralize any free acid that may be formed on storage. In finished smokeless powder, such an addition would be contraindicated, as it would increase the solid residue in the gun, and cause some smoke.

It will be recalled that guncotton, as it leaves the hydraulic press in its last stage of manufacture contains about 15% of moisture, or if from centrifugal drying, about 21%-31% of moisture, depending upon the time and speed of wringing. In this condition, it is inflammable in proportion to the water contained therein, and explosive by means of an ordinary fulminate. However, it is very readily detonated through the agency of cumulative detonation (the method first enunciated by H.

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abst. J. S. C. I. 1898, **17**, 1179, 1180; 1899, **18**, 174; 1907, **26**, 840; Chem. Centr. 1899, **70**, I, 76, 509; 1907, **78**, II, 955; Jahr. Chem. 1898, **51**, 1379; 1905–8, II, 980.

[1] J. S. C. I. 1897, **16**, 283; Zts. ang. Chem. 1897, **10**, 233, 265; abst. Mon. Sci. 1898, **51**, 37; Chem. Centr. 1897, **68**, I, 1185, 1186; Jahr. Chem. 1897, **50**, 1064; Meyer Jahr. Chem. 1897, **7**, 300; Wag. Jahr. 1897, **43**, 487.

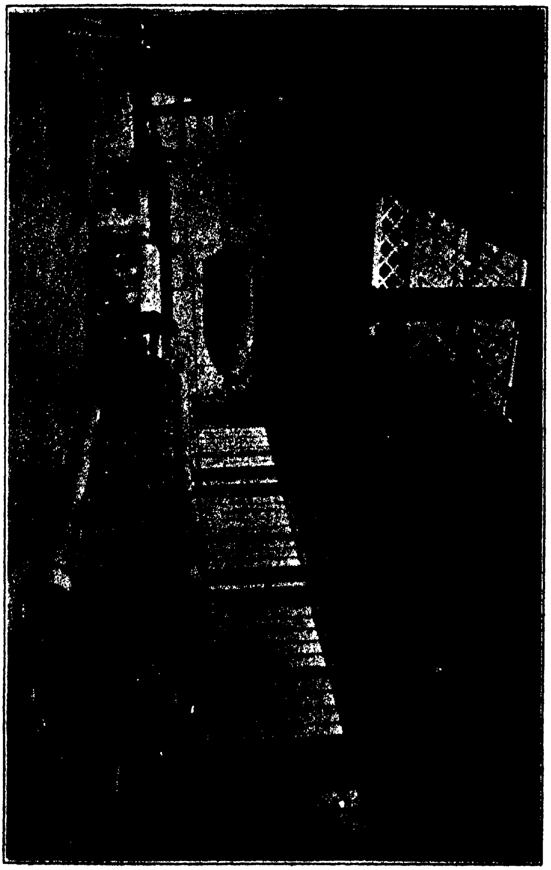

FIG. 263.—BLOCK OF GUNCOTTON AND PRESS

Sprengel),[1] an effect originated by or through the initial explosion of the detonator surrounded by an envelope of dry guncotton.

The exploding detonator acts similarly to that of an envelope of dry guncotton, and the force thus accumulated or multiplied, causes the explosion of an unlimited quantity of wet guncotton with which the cumulative detonator may be in contact.

This fact has attained a high degree of practical importance, and in no small measure, has contributed to the use of guncotton safe for military and naval purposes. It permits the storage of the main bulk of guncotton in a wet, and hence non-inflammable condition for any reasonable length of time, and without danger so long as the moisture is not removed.

The specifications for guncotton slabs for mines, differ but comparatively little in the various countries for nitrocellulose intended for a specifically named purpose. Those of the British Government, may be considered typical, and are said to be as follows:

1. The guncotton is to be manufactured from cotton or cotton waste.

2. The percentage of nitrogen is not to be less than 12.8%, nor more than 13.1% as calculated on the dry guncotton.

3. The percentage of organic matter insoluble in acetone should not exceed 1%, but some contracts have been made on a 2% insolubility.

4. The total alkalinity calculated as percentage of $CaCO_3$ is to be within the limits of 0.8%-1.5% on the weight of the dry guncotton.

5. The guncotton is to be free from grit, and is not to contain any substance other than that naturally present in cotton, or unavoidably taken up from the water and the machinery employed in manufacture. The total mineral matter is not to exceed 3%.[2]

6. The guncotton, either in the form of pulp, or when com-

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[1] J. C. S. 1873, **26**, 806; abst. Amer. Chemist, 1873, **4**, 174; Bull. Soc. Chim. 1873, **20**, 257; Dingl. Poly. 1874, **212**, 323; Poly. Centr. 1874, **40**, 970; Wag. Jahr. 1874, **20**, 434; Jahr. Chem. 1873, **26**, 1031; Proc. U. S. Nav. Inst. 1873, **26**, 796; Chem. News, 1875, **31**, 9; Phil. Trans. 1874, 362.

[2] The most suitable method of adding alkaline matter will probably be found to be as follows; After the pulp has been washed, sterilized and purified in the usual way, the wash water is to be removed and so much of a clear saturated solution of lime water is to be added as will give, as a final alkaline content, the prescribed amount. The pulp is to be thoroughly

FIG. 264—COMPRESSION OF GUNCOTTON INTO BLOCKS

pressed into primers or slabs, is to stand a heat test of not less than 10 minutes at 76.7°, when conducted as recommended.

7. The primers and slabs are to be made of finely pulped guncotton submitted to a pressure of not less than 4 tons per sq. in. of surface, and of dry weights and wet dimensions as specified.

8. The primers and slabs should contain by weight, not less than 14%-16% of water per 100 parts of dry guncotton.

9. The primers and slabs are to be free from any tendency to split or open up.

According to O. Guttmann,[1] in the employment of nitrocellulose of 12.3% nitrogen or thereabouts:

a. Cartridges of equal diameter but of varying heights exert approximately equal effects.

b. Cartridges with hollow center are more effective than solid ones of the same diameter.

c. Moist guncotton is more effective than dry, and addition of barium nitrate increases this effect.

d. The larger the sectional area of the cartridge, the more widely spread its effect, the direction of propagation of which is determined by the area of the base of the cartridge.

e. Maximum effect is produced by initiating the explosion on the side farthest removed from the object, or by hollowing out the cartridge on the side nearest the object.

Of these pressed guncotton masses, the cylinders for blasting cartridges vary considerable in diameter, the height being, 5, 7, and 10 cm., the cartridges being wrapped in paper after pressing, or they may be pressed directly into paper shells. Guncotton prisms are usually quadrangular (4 × 4 × 7 cm.) or hexagonal prisms, the latter in two general sizes, 8.1 × 5.5 cm. and 7.4 × 5 cm. being produced. The latter size is usually produced of unusually high density (1.15-1.22). For stationary sea mines, prisms of $^1/_4$-$^1/_2$ kilo are frequently used. The Austrian torpedoes are made cylindrical, while the German torpedoes are more often conical. The cylindrical bodies are either prepared by placing cylindrical guncotton slabs one upon another, or

stirred up in this lime water, and a solution of carbonate of soda, sufficient to precipitate the whole of the lime, is to be added; the pulp is then to be again well stirred up. After the stirring, the soda salts are to be removed by at least three washings.

[1] Dingl. Poly. 1883, **250**, 456; abst. J. S. C. I. 1884, **3**, 329; Chem. Ztg. 1883, **7**, 1696; Chem. Tech. Rep. 1883, **22**, II, 188.

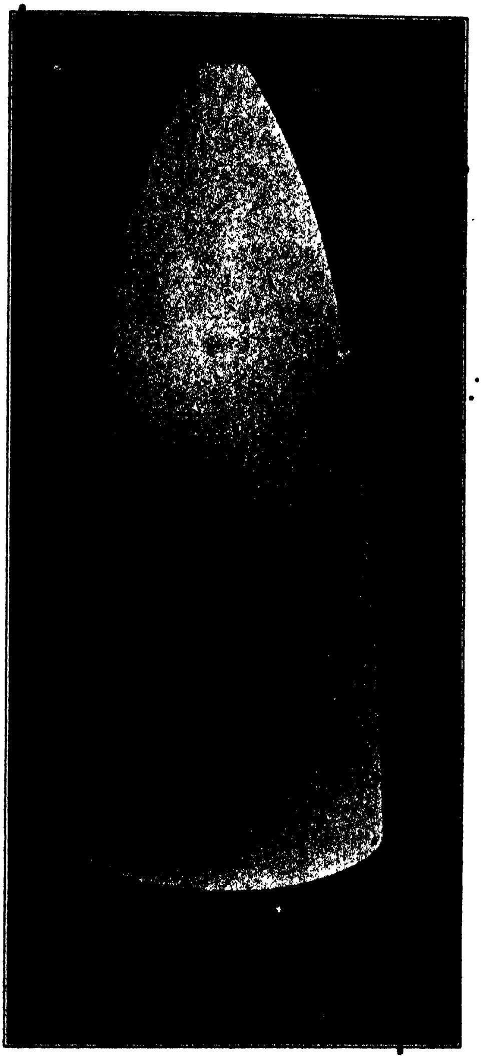

FIG. 265.—GUNCOTTON BLOCK

radially divided slabs are used with a center piece, as has been described.

The conical bodies are similarly formed, a canal being provided for the insertion of the detonating charge. These bodies are used for filling the head part of the fish-shaped torpedoes. Guncotton being elastic, an expansion up to 3 mm. is observed after normal pressing, in the direction in which the maximum pressure has been applied.

The pressed guncotton exhibits a laminated-like structure, vertically to the direction of maximum pressure. On the surface it appears more like a skin, or where small amounts of solvents have been employed for exterior indurating, the surface may take on a corneous texture and horny appearance.

Pressed guncotton bodies can be milled and worked on the lathe similar to wood, by sawing, drilling, turning, rasping and scraping, but it is necessary that an abundance of water drip on the guncotton mass while manipulating it as above, in order to guard against the possibility of sparking by friction.

The drilling of guncotton is a frequent operation. For canals up to 4.5 mm. center drills are used, below this special drills, and for diameters of 10 mm. are turned out. The guncotton mass may be placed in a vicelike device for boring, as there is a distinct tendency to peeling, especially if the slab has not been uniformly compressed. In drilling, water is allowed to continually drip on the drill, the latter being raised from time to time, rather than kept down continuously.

For filling small spaces with guncotton, granulated nitrocellulose is often used on account of the too great difficulty in working small nitrocotton bodies. For such uses granulated guncotton is more suitable, the granulation being accomplished as detailed in another topic herein.

Nitration of Cellulose in Great Britain. At Gretna and at Queen's Ferry, both being government controlled plants, the nitration of cotton was carried on during the war on a huge scale, and to a high degree of perfection. The methods employed and the details of the steps of manufacture are illustrative of the best and most recent approved practice, as carried out in this country, and are, therefore, given somewhat in detail herein.

Nitration of Cellulose at Gretna. *Outline of Process.* This section of H. M. Explosives Plant at Gretna, Scotland, was divided into the following five departments:

1. Cotton Waste Bale Stores, in which the bales are delivered from the manufacturers. The material is weighed on entering, and from which it is issued to process, in which state it contains about 7% of moisture.

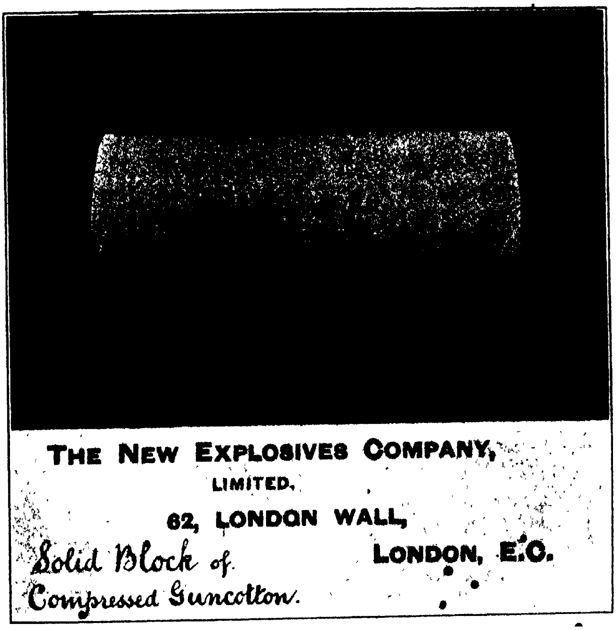

FIG 266

2. Cotton Waste Treatment Department, where the bales of cotton waste are broken open, the cotton teased and cleaned free from foreign material, dried, weighed and issued in definite quantities to the nitrating house.

3. Nitrating House, in which the Thomson displacement process is used exclusively, and where the purified cotton waste is dipped in the nitrating bath in the ratio of one part cotton to

32 of mixed acid. After the elapse of the specified nitration period, the residual acid is displaced with cooled water, and the former, revivified, distilled or discarded.

4. Boiling House, wherein stabilization by boiling is carried out. The nitrocotton here is subjected to a series of boils, consisting of two long boils in acid liquid, and three shorter boils in alkaline liquid.

5. Heating, Poaching and Wringing Houses. The boiled nitrocotton is finely cut in beating machines, the grit removed by blankets, the iron by magnets, and any residual long fiber by combs. The nitrocotton is then poached, calcium carbonate added as a stabilizer, after which it is blended into lots and wrung

The cotton waste bale stores and waste treatment processes have already been described (see p. 642).

Nitrating House. The dimensions of the nitrating house was approximately 432′ x 78′, with a 6″ slope on floor, and contained 644 Thomson nitrating stoneware pans (see Figs. 267–269), the pans being arranged in sets of four, with 4′ 1″ between centers, and seven sets in a row. Distance between rows, 18 feet. The average dimensions of the individual pans are: Internal diameter, 3′ 9″; depth, 11$^1/_4$″; capacity sufficient to take a charge of 27 lbs. cotton waste and 877 lbs. mixed acid. One row has been equipped with large pans, 3′ 9″ diameter and 14″ deep, which will accommodate a charge of 34–35 lbs. cotton waste.

The acid enters the house through 2$^1/_2$″ branches from a 4″ iron main, the pans being connected to the branches through a 1$^1/_2$″ earthenware cock. The spent acid is drawn off through a $^3/_4$″ lead star pipe to either of two 3″ earthenware mains, the plant being so arranged that either one spent acid, or strong acid and weak spent acid can be collected.

All spent mains are protected with iron rail and wooden covers. The 3″ mains lead into 4″ mains outside the nitrating house. The fumes arising from the dipping are drawn off through 6″ earthenware uprights from 9″ earthenware pipes running along the center of each row. These connect to a 15″–21″ main outside the house, leading to the ejector fans. The cotton waste bins are conveyed into the house on Slingsby trucks—six bins per truck. The nitrocotton is conveyed out of the house in aluminium or galvanized iron lipped buckets on six-wheeled

Fig 267 —Unpulped Nitrocellulose

bogies, a load of nitrocotton comprizing the contents of two pans (86.4 lbs. dry weight).

From nitrating to the vat house conveyance of the buckets is by means of a Vaughn overhead runway, with one ton conveyors, the number of conveyors required being 18, and the number of buckets 24.

Acid Storage. The mixed acid storage tanks (16 in number) of $^1/_2''$ mild steel, two being lead lined, this arrangement permitting of ample storage of both strong and weak spent acids. Each tank is provided with a dip-rod gantry, the outlets fitted with Regulus metal safety plugs, Quinan valves and cast iron gland valves, the capacity being 180 tons per tank.

Mixed Acid Temperature Regulation. The temperature of the mixed acid entering the nitrating house is controlled by passing it through six sets of coils in parallel, each set consisting of four $1^1/_2''$ wrought iron coils, one inside the other, standing in a cast iron tank. Steam, service water and refrigerating water can thus be turned on as required, the acid passing from the coils through a condenser, through which cooled water flows.

Spent Acid Pump Houses, consists of two houses, each containing four tanks and four pumps, the latter being driven at a speed of 1440 r. p. m. from a shafting motor driven, situated in an annex to the nitrating house. The motors are 10 h. p., with 740 r. p. m.

The tanks are each 8′ diam. x 2′ 11″ deep, set in a well 30′ x 39′ 6″ x 3′ 5″, the floor of which has a one-inch slope to the back. A small steam ejector is used to carry away seepage and spills. Power consumed, 10 kilowatts per hour.

Ejector Fans. Two large induced-draught fans, 13″ nozzles each, connected to six rows, and driven by 20 h. p., 980 r. p. m. direct coupled motors, running at 26 amps., with an average draught of $1^1/_2''$ in the house. The power consumed being 4 kilowatts per hour. In addition there was provided 4 small induced-draught fans, 6″ annular nozzle, each pair connected to six rows, with a 10 h. p. 1440 r. p. m. motor, giving an average suction of $1^1/_4''$ water gauge. Power consumed, 2 kilowatts per hour. The Sirocco fan was here omitted.

Vat House. This is a sheet-iron building containing 126 vats, in rows of six, the rows being equally spaced, the vats being fed by an overhead runway, leading from the nitrating house through an electric lift situated at the center of the building, or through a hydraulic elevator situated at the north end of the building. The electric lift working cycle was 65 seconds, with maximum capacity of 255 tons per six-day week, as against a capacity of 380 tons for the hydraulic lift during the same period. The runway from the lifts is carried down the side of the house, and branches lead off to the various rows of vats, one branch serving two rows. This necessitates the use of a chute in loading, the latter being made of wood, is moved about from vat to vat as required (see Fig. 270).

The vats stand on beams 18″ above an asphalted concrete floor, the working floor being of pitch pine, and 15″ below the top of the vats, the latter having a capacity of 2500 gal. of water. The vats are of 3″ pitch pine, tapered, with mean diameter 9′ 3″, average depth 6′ 3″, of which 125 are provided, with foundations for a further 30. The capacity of each vat is 2.157 long tons per charge, with an approximately 65-hour cycle. Allowing 5% out for repair, the capacity of the house would be 350 tons of nitrocotton per 7-day week.

The water supply is either drawn from the glycerol distillery condensers, any deficiency being made up by water from the condensers in the refrigerating plant during the summer, or from the main in winter. The water consumption is about 17,000 gals. per ton of finished nitrocellulose product.

Steam Supply. The steam inlet is through a $1^1/_4''$ pipe, changing at vat to 1″ lead pipe with gun-metal union, the pipe being carried to the center of the vat, where it turns up 3″ with full bore opening. Steam pressure, 65 lbs.; steam consumption, 15 tons per ton nitrocotton.

Over the steam nozzle a round, tapered wooden column stands, built up of six segments, having flat, internal faces to form a hexagon internally, and bound by lead covered, iron bands, and with $5^1/_4''$ distance between faces. The column, the length of which varies with the vat, stands on a lead pedestal with openings in each direction to serve as water inlet, and provided with a wooden cap with $1^1/_4''$ clearance from top, to serve as circulation outlet. The floor of the vat is flat, so that drainage is slow. Six inches above the floor is a spaced false

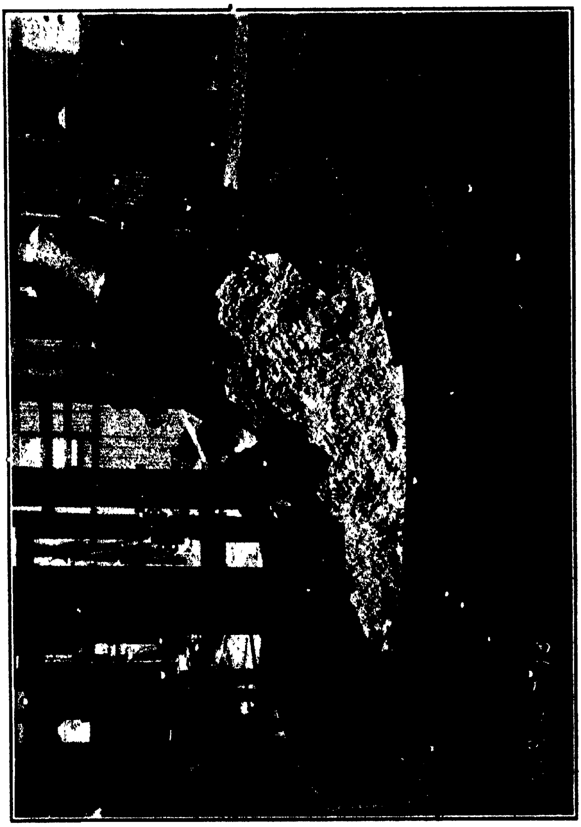

FIG. 270.—BOILING THE NITRATED CELLULOSE

bottom carried on bearers, upon which the nitrocotton rests, water being sucked through it into the central column for circulation.

Overflow. A lead chute outlet leads from the top of the vat, which carries displacement water to waste.

Steam Flue. A wooden flue 8″ x 8″ internally, carries to waste, exhaust steam used for circulation, being provided with a damper in the flue which is kept in position while the vat is coming to boil, but withdrawn during actual boiling, thus keeping the building substantially free from steam.

Discharge Runway System. This is distinct from the charging runway system, so that the buckets cannot cross from one line to the other. There are provided two exit lifts, one electric and one hydraulic—the former being at the center, and the latter at the end of the building, and are on the opposite side of the house to the inlet lifts, being provided with a separate branch to each row of vats, but on the opposite side of the vats to the loading, so that one side of the vat is reserved for loading, and the other side foi discharging. The buckets—of maximum full load weight of 600 lbs.—are brought to and from the vats by one-ton conveyors.

Beater House Elevators. It happens that the beater house floor is 7′ 9″ above the floor of the vat house, so the buckets conveying the nitrated cotton have to be carried up by elevators—one electric and one hydraulic. The cycle of the former is 60 seconds, with a two-ton per hour capacity, while the hydraulic lift is 45 seconds, with a 380 ton capacity per week.

Beaters. The capacity of the individual beaters depends upon the nature of the cotton waste nitrated, on the condition of the bed plate and roll, and upon the power available. The maximum obtainable has been found to be 0.095 long ton per machine hour with a 0.19 ton charge, and a two-hour cycle, while the working capacity is 0.08 ton per machine per hour, equivalent to 300 tons per 6-day week for the 26 beaters there installed (see Figs. 271 and 272).

The driving motor is 30 b. h. p., 42 amps., 720 r. p. m. but is usually run at 60–63 amps. (i. e., 38–40 b. h. p.); during beating, however, the belt drive from a 13″ pulley is 190 r. p. m. The drum is raised or lowered by means of a worm wheel acting

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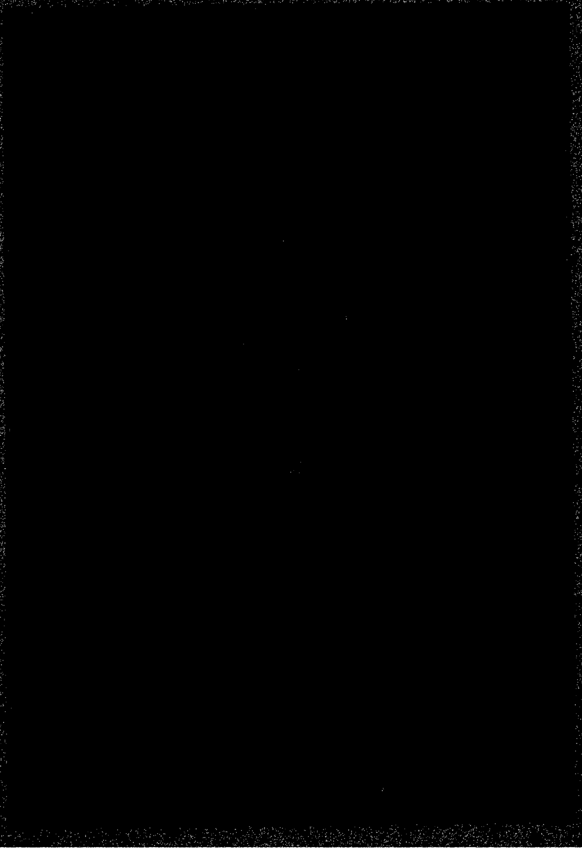

on a lever, an ammeter being directly opposite the lowering device to indicate the power being consumed. The bedplate contains 22 to 24 elbowed knives, while the roll has 66 straight knives in sets of three.

Water Consumption. The water supply is 4", with patent rubber cushioned valve, which is placed immediately over the running-off inlet, the water consumed in beating being 30,000 lbs. per ton, with a power consumption of 480 kilowatts per ton.

Outlets. There are two outlets, one 8" opening leading to the stuff chest launders, and a 4" opening leading to the long fiber save-all, the latter being for cleaning down the machine.

Stuff Chest Launders, are of aluminium, 20" wide and 10" deep, there being two. The one from the side of the house and leading to the stuff chests, can be baffled so that 6 to 8 beaters lead to a single stuff chest. The other launder collects from the other side of the house, and in the same manner delivers to other stuff chests.

Stuff Chests. Eight in number, are located on the ground floor in the center of the building, and serve as intermediate storage tanks, with a capacity of 0.25 ton nitrocotton per chest, being 6' deep and 7' diameter with truncated conical agitators driven by 4$^1/_2$ h. p. motor, the speed of the agitator being 55 r. p. m. The outlet is through a Quinan valve to 3" centrifugal pumps directly coupled to 8$^1/_2$ h. p. motor, 12.3 amps., and 1420 r. p. m., delivering into a distributing box with overflow outlets to grit separation launders. The gradient of the run is 1/100.

Grit Separation Launders, consist of aluminium trays 4" deep, 21" wide, and which are paved with blankets, or better, lined with permanent cross baffles for catching sand and grit as the nitrocellulose pulp is pumped from the stuff chests to the top end of the launder or sluice, and run by gravity down the launder. The author can attest to the efficiency of this arrangement, from personal observation at this factory. Four sets have been installed. Four stuff chests deliver into two sets, and the other four into the opposite chests, one set being usually in use while the other is baffled off for cleaning. Each set consists of an upper launder running from the center of the house to the end, where it meets the delivery launder from the grit tanks, at which meeting point is a rectangular chute 12" x 3", delivering into a distributing box 18″ below the level of the upper rim. From the box are provided two overflows into launders similar to the above and these run back to the center of the building. They are in, 12 feet lengths, with grit traps between each two lengths, the latter being small sumps with cleaning outlets delivering into a V-trough which leads back to the end of the house, and delivers into a washing box.

Magnets. The launders finally end in a grit trap, from which they unite in a aluminium baffled trough, which overflows on to two magnet trays, either of which can be baffled off. The magnet trays consist of boxes 6′ x 2′ x 6″ deep, lined with copper, and containing 16 rows of electromagnets 2″ wide and 2′ long. At the end of the tray is a chute pivoted on to the box, and balanced so that normally it delivers into a launder leading to the potchers. If, therefore, the current ceases to flow so that the magnets cease to functionate as such, the chute falls, and the delivery is changed to the grit tanks for re-work. At the same time a bell is brought into circuit, and its ringing gives the necessary warning. The current for the magnetic separators is 100 volts, direct current. The magnetic separators may be obtained from the Rapid Magnetizing Co., Birmingham. The capacity of the grit separation launders is 1.25 tons per hour per set; allowing for two sets running continuously, while two sets are cleaning, gives a capacity of 2.5 tons per hour, equivalent to 310 tons per six-day week.

Washing Boxes, of which one is provided to each half of the poacher house, are each 6′ long x 2′ wide x 1′ 9″ deep, with an overflow partition 1″ from the end. In the longer part of the box is a decanting outlet leading to the dirty grit tank. In the shorter part is an overflow outlet leading to a clean grit tank, and a cleaning outlet leading to the dirty grit tank. On top of the partition is a sieve for filtering out the long fiber nitrocotton.

Blanket Washing Boxes, are similar to those described above, but are kept exclusively for washing blankets, being steam-heated. They have scrapers fitted to the sides for the cleaning of the blankets.

Blankets used are raised white cotton moleskin 21″ wide, which are laid on trays and held in position by means of lead bars.

Long Fiber Combs. These combs are lead-weighted wooden boards containing 150 projecting 3″ brass screws, and are located in the grit runs where they entangle the long fibered nitrocotton as it passes.

Grit Tanks. Two tanks to each half of the house, one for the relatively clean nitrocellulose, and the other for the relatively dirty. They are iron tanks 7′ 6″ x 4′ x 4″, in the outlet to which is a 2″ pump direct coupled to a 3 h. p. motor, at 1400 r. p. m. This pump delivers to upper feed launder at the end of the poacher house, and thus direct to the lower launders.

Poachers. After the nitrated cotton has run down the grit launders and over the magnets, it delivers into an aluminium launder which leads to a wooden lead-lined launder 10″ wide and 9″ deep. The two launders (one from each set of magnets) meet and run side by side to the center of the stage, from which point each branches down half of the house to supply eight poachers. Where they meet interconnection is provided, so that a beater can be delivered to any point on the poacher stage, the delivery being controlled by gates. There are also gates at the inlet of each machine. The poachers themselves are large iron washing machines, capable of treating one ton of nitrocotton at a time. At one end of the machine is a 6″ centrifugal circulating pump, belt driven at a speed of 450 r. p. m. by means of a 25 h. p. motor. Delivery from this pump is through a long narrow slot or nozzle 1$^1/_2$″ x 3′ 10″ into a chute at the other end of the machine. This gives to the nitrocotton in the poachers the necessary circulation for washing, after fresh water has been added.

Three inch pipes for decanting off the dirty water are provided, swivelling on a loose union attached to the bottom of the poacher. They are provided with a cross piece of 3″ piping with a $^1/_4$″ slot for draining off the liquid, this cross piece being teed on to the main arm. The whole is counterpoised more or less by means of a lead weight. Below the poacher, these pipes lead into wooden launders delivering into the save-all.

The pulp outlet is 9″ and delivers into 9″ mains leading to a 6″ centrifugal pump with a branch to the save-all for cleaning purposes. The pump is direct-coupled to a 42 h. p. 1440 r. p. m. motor, there being one pump and motor to each half of the poacher house, being interconnected, so that, if necessary, any poacher can be sent to any blender, and one pump thus becomes a spare to the other, of value in case of accident.

Capacity of Poachers. A charge of 1.08 (long) tons, and a cycle of 7.5 hours, gives a capacity of 0.144 ton per machine per hour. Of the 16 machines employed, assuming 15 of them to be continually in action, admits of the treatment of 305 tons per six-day week.

Blending Tanks are 21′ diameter, 6′ 6″ deep, with a capacity equivalent to 4 tons of dry nitrocellulose, being six in number. Each is provided with a hollow truncated conical agitator, driven by 17 h. p., 930 r. p. m. motor, geared down to a speed of 20 r. p. m.

Wringer Feed. Outlet leads to the suction of a 4″ centrifugal pump driven by a 10 h. p. 720 r. p. m. direct-coupled motor. Delivery from the pump is around the rear of the centrifugal machines, and thus up to the top of the blender. Between each pair of wringers is a 3″ Quinan valve with a short hose pipe on nozzle, connecting it to a 4-way distributor suspended on a swivel arm. Strainer bags 3′ wide and 3′ 3″ deep are suspended from and filled through this distributor into centrifugal machines (Figs. 273–275).

Capacity of Tanks. Six tanks with a 6-hour cycle, and a charge of 4.32 tons, are provided. The capacity, therefore, is 1.44 tons per tank hour, a total of 1000 tons per six-day week.

Wringers. There are 24, in three banks of eight, and are water driven. The high-pressure pumps are driven by direct-coupled 105 h. p. motor to deliver water at 200 lbs. per sq. in. Two pumps are provided to each bank of 8 wringers—one acting as a spare to the other. The spent water is returned to a tank, from which pump again draws its supply. The machines are driven at a speed of 1000–1100 r. p. m., the baskets being 42″ diam., accommodating a charge of 0.055 ton per machine hour. There are 24 machines installed, and on the assumption that 16 are running on a 20-minute cycle, the total plant capacity is 330 tons per six-day week.

Weighing. Twelve bags are weighed at a time on a one-ton scale, and trucked to the screening house.

Save-All consists of a long settling drain, divided into two sections—one for nitrocotton contaminated with long fiber, and one for nitrocellulose free from long fiber. The settled nitro-

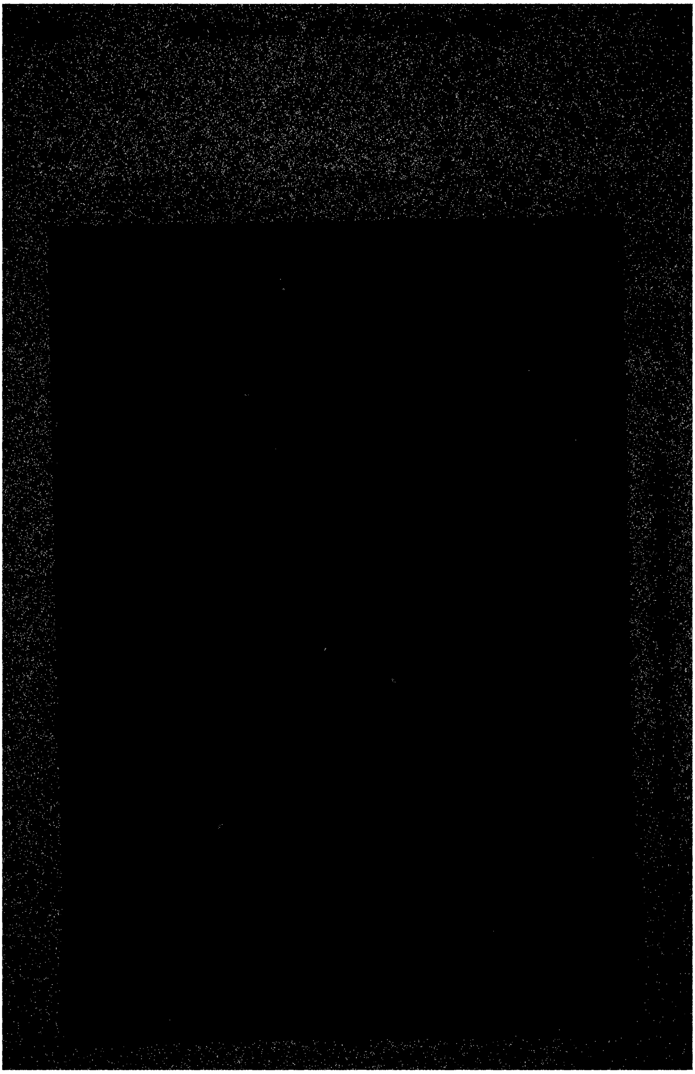

FIG. 275.—PICKING OVER THE NITROCELLULOSE

cellulose from the latter is pumped into the re-work tank with a 3″ pump, direct-coupled to an 8½ h. p. motor, the suction having a flexible hose connection with a sieve on the end of it.

Re-work Tank, is a wooden, lead-lined tank 8′ long x 8½′ wide, and 4′ deep, divided into three compartments. The first compartment is 2′ long and 8½′ wide, being 6″ above the floor of the tank, through which the nitrocotton flows into a second compartment. The latter is 4′ long and provided with an agitator. Between the second and third compartments a partition rises to 9″ from the top, being provided with a sieve, through which the nitrocotton must flow into the third compartment. This is 2′ long with an outlet to a 3″ pump direct-coupled to an 8½ h. p. motor. This pump delivers into a switch box over the grit separation launders, while the box has gates; launders delivering to either set of grit runs. The beater and poacher motors are air-cooled, while all centrifugal pumps are fitted with water injectors into stuffing boxes. All the motors on the ground floor driving machines and the pumps on the upper floors are fitted with emergency switches and signal lights. The whole building, including the motor floor, is in the "clean area," with floors of gritless asphalt.

Detailed Description of the Process. The following is a detailed description of the process in its entirety, from the raw cotton to the finished and inspected nitrocotton, in general, as carried on at the Gretna plant, including methods of procedures not touched upon in Chapter IV of this volume.

Cotton Waste Treatment. The trucks of raw cotton waste from the waste mills are run into the stores and off-loaded with overhead hand-cranes, care being taken that all consignments of cotton waste are kept separate and labeled. The cotton waste is issued to a requisition from the process engineer in charge of the department, stating the number of bales required from each consignment for the day. Consignments must be passed by the factory chief as within specifications before being drawn.

Specification for Cotton Waste for Cellulose Manufacture. The specifications direct that it shall be *cotton* cellulose, specially suitable for the manufacture of nitrocellulose, to consist largely of fibers of long staple, preferably twisted, and to contain as little as possible of felted, unspun short fiber cotton or dust, technically known as "fly." Spun material, such as cops or cop bottoms, may not be used. Weaving mill waste may also not be employed.

The waste must not show more than the following figures calculated as percentage on the dry material:

Moisture	7.0%
Oily matter	0.6%
Soluble on boiling 1 hr. in 3% NaOH	5.0%
Reduction of Fehling's solution (1 vol. to 2 vols. water) on heating 15 mins. at 100°	1.0%
Mineral matter	1.25%

Except as regards the above figures, it must be entirely free from organic matter other than pure, resistant normal cellulose, and on dyeing with a basic dyestuff as fuchsine, the fixation of color must be slight and uniform, and must show no deeply dyed particles or fibers.

The consignments are blended to quality and date of receipt, each bale being weighed on the run-way weigh-bridge at the time of issue. All the work in connection with the receiving and issuing of bales is in charge of the Stores Department.

Bale Breaking. A stock of bales is brought over each day to supply the three shifts, there being available space in the bale breaking room for 100 bales. The bales are broken out of the stack, placed on small bogies and run to the bale breakers, where the straps are cut with a strap knife and the wrappings removed. All straps and wrappings are collected and returned to the cotton waste mills. The breakers open up the cotton waste and remove large quantities of husk, wood and sand, which are caught in a tray beneath the machine, being periodically removed and burned.

Teaser Feed. All fly and dust are removed through a fan to a cyclone, the cotton waste leaving the machine falls into a hopper, and is conveyed by means of a fan through a 16″ pipe to the teaser feed. One breaker supplies three teasers, the cotton waste being distributed by means of a flap valve. The rate of feed is controlled from the teasers by means of a bell signal. All dust and fly caused by the air conveyor are removed by a suction fan and cyclone.

Teaser. From the feeder the cotton waste issues in an even layer to the teaser, where it is opened up and largely freed from foreign matter. The waste from this machine is all re-treated in the re-work willower, and a considerable saving effected.

Drier. From the teaser the cotton passes up an elevator brattice and falls on to the top brattice of the drier, travels the length of the machine, drops to the next brattice, and so on over the five brattices, then through the willower, which again opens up the cotton waste—freeing it at the same time from foreign matter and short fiber cotton, and delivers it through a two-way feed into bins—one bin being placed in position while the other is being stacked. The cotton waste is dried by a current of air heated to 100°, by being blown through a tubular steam heater under the drier. The time required to pass through the drier is $9^1/_2$ minutes with a 10″ driving pulley.

Moisture Content. During the passage of the cotton waste through the drier, the moisture is reduced from 7%–10% to 0.5%–1.0%. The charge of cotton waste per bin is adjusted on a platform weighing machine to 27 lbs. dry weight ($^1/_4$ lb. being allowed for moisture). The bins of cotton waste are stored in the cooling room for 3–4 hours to allow the temperature of the waste to fall to about 20°. The number of bins required in continuous use is about 500.

Fire Service. The department is fitted throughout with Mather & Platt automatic sprinklers, and hand hose and fire extinguishers are situated at convenient positions. The driers are equipped with a water drenching system of twenty $^1/_2$″ pipes from a $2^1/_2$″ supply, and a steam drenching system of $^3/_4$″ pipes. The willowers have a separate set of three water jets. Special girls are detailed to each shift to attend to the various fire duties.

Nitration. The bins containing 27 lbs. of cooled, dry cotton waste are trucked to the nitrating house and placed along the wall at the top end of the rows. Aluminium hoods are placed on the set of nitrating pans to be dipped, and connected to the fume main with aluminium four-way connections. The outlet plug is removed, the set completely drained, and the plug replaced.

Mixed Acid. Aluminium gauges are placed on the sides of the pans, and the acid runs up to the bottom of the gauges. The quantity of acid is regulated to give a ratio to cotton of 1:32.5. The acid specifications may be stated as, sulfuric acid, 62.14–62.17; total nitrogen acids, 22.85%–23.15%; water, 14.8%–

14.9%, varying slightly according to the season of the year.

Dipping. The bins of cotton waste are rolled into position in front of the pans, the gauges removed, and the cotton waste dipped under the surface of the acid in small armfuls with aluminium forks.

Sealing. When the entire charge has been completely immersed, earthenware, segmental top plates are put over the surface of the cotton and a thin layer of water to keep down the fumes is run over the surface through rubber tubes. This water is cooled to below 10°. The empty bins are rolled back to the wall, and returned to the cooling room. While dipping is in progress at one set, the next set is fitted with hoods and filled with acid. On finishing a set, the dippers transfer the hoods to the next set to be filled, and the acid runner finishes the connections.

Displacement. The cotton waste is allowed to nitrate for 2 hours, 10 minutes, and then the acid is displaced, the water distributor is turned on, and the outlet cock opened. The spent acid is run off through a lead siphon down the spent acid main to the pump house, and from there pumped to storage tanks. From the latter, it is either taken for revivification or distillation.

Spent Acid. The average composition of the acid obtained is sulfuric acid, 61.1%; nitric acid, 19.8%; water, 19.1%, from which it will be observed that the sulfuric acid decreases about 1%; nitric acid decreases about 3%; and water increases about 4.2% as the result of the nitration.

The level of water during the displacement is maintained just below the top of the pans. When the sp. gr. of the spent acid decreases to 1.200—as indicated by the hydrometer float in the sight glass sinking—the water is turned off and the set drained to waste for ten minutes. The top plates are then removed, and the nitrocellulose lifted out into aluminium buckets, which are conveyed on bogies to the runway, and hoisted to the vat house by means of an electric elevator.

Treatment of Spilled Cotton Waste and Nitrocotton. Cotton waste spilled while dipping is picked up, and if dry, dipped in the next set; if wet, placed in a tub at the end of the row to be transferred to the waste bin at the end of the shift. All nitrocotton spilled is picked up, and, if reasonably clean, placed in the buckets; if too dirty, it is placed in a tub at the end of the row.

All waste is weighed, and each shift debited with its own loss. The girls are supplied with clogs and the usual khaki uniform; while those on dipping, displacing and acid running, receive rubber gloves, rubber aprons and aspirators.

Pan Cycle. Running up acid, 15 min.
Dipping cotton waste, 15 min.
Nitration, 2 hrs. 10 min.
Displacement, 2 hrs. 30 min.
Discharging, 10 min.
Total, 5 hrs. 20 min.

Stabilization. The nitrocotton rag enters the vat house by means of two runways, one ending in an electric elevator situated at the center of the house, and one ending in a hydraulic lift situated at one end of the house. From there, buckets are delivered to the vats via the branch runways. At the vat, the false bottom is covered with water and then the bucket contents are emptied into it by means of a chute. Thirty buckets, or 15 sets, constitute a vat charge—equivalent to about 1.157 tons—and this, for record purposes, is termed a consignment. The ratio of nitrocotton to water is 1. 10. Water is then run in to within two feet from top (to allow for expansion and condensation), and the steam is turned on.

Water Treatment. The water used in the stabilization process is alkaline to the extent of 0.014% as calcium carbonate, the alkalinity of the main supply water varying from 0.003%-0.012%. This water is regularly tested every two hours, and the quantity of sodium bicarbonate to be added, being dependent upon the results of this determination. A definite quantity of water is run into the mixing tank, and the calculated quantity of sodium bicarbonate added. Agitation is allowed to proceed for two hours, after which the charge is dropped into the storage tanks. Two charges can be made upon the one shift, giving a sufficient quantity to last for the 24 hours. The concentration of the charge varies, of course, according to the alkalinity of the supply water, but the mean figure is about 3%, calculated as $CaCO_3$. One man on the day shift is able to keep the plant running satisfactorily.

Time Table of Boiling. The nitrocotton is usually submitted to a minimum of five distinct boils, arranged somewhat as follows:

First Boil. Of 12 hours, after which a sample is taken and titrated against N/NaOH. If the result be within specification limits, the outlet is opened and the vat drained for one hour. The acidity after this first process boil is recorded on a process record sheet, the mean figure being 0.12% sulfuric acid.

Second Boil. Of 12 hours, after which a sample is taken and the reaction to methyl orange determined, after which cold water is run in at the bottom, so that the hot water overflows at the top, the time of displacement being approximately two hours. The level of the water is dropped two feet before again turning on the steam. Mean acidity, 0.03% H_2SO_4.

Third Boil. 6 hours, the reaction after this boil being noted, and generally found to be 0.00075% H_2SO_4. The nitrocotton is then drained for one hour.

Fourth Boil. 6 hours, reaction generally alkaline to the extent of 0.00075% NaOH. Drain for one hour.

Fifth Boil. Similar to the fourth. After boiling, displace by cold water, drain, and the vat is ready for discharging. The liquor from the last boil is titrated, and entered on a permanent record.

Discharging. Before commencing to discharge, the process record sheet is checked by the chemist on duty, and when satisfactory, the buckets are lowered into the vats (see Fig. 276), filled, and hauled out again by hand, being conveyed on a runway to the beating stage, as shown in the photograph.

Picking. On the beater stage the buckets are dumped on to the tables and the rag is picked over and teased to the beaters. The latter is first filled with a definite quantity of water (usually 4000 lbs. are $8^1/_2''$ from the top) to give a ratio of from 1:13 to 1:14 on the nitrocotton added. All pickings are dropped into a small bag suspended from the table. The motor is then started and the nitrocotton fed in as rapidly as possible, the ammeter showing full load on the motor during charging. When all is in, the roll is steadily lowered until a 50% overload is registered, the indicator being kept at this point until the beating is completed.

Charge. Five buckets (0.18 ton) constitute a beater charge. There are four to six vats discharging at once, and the buckets

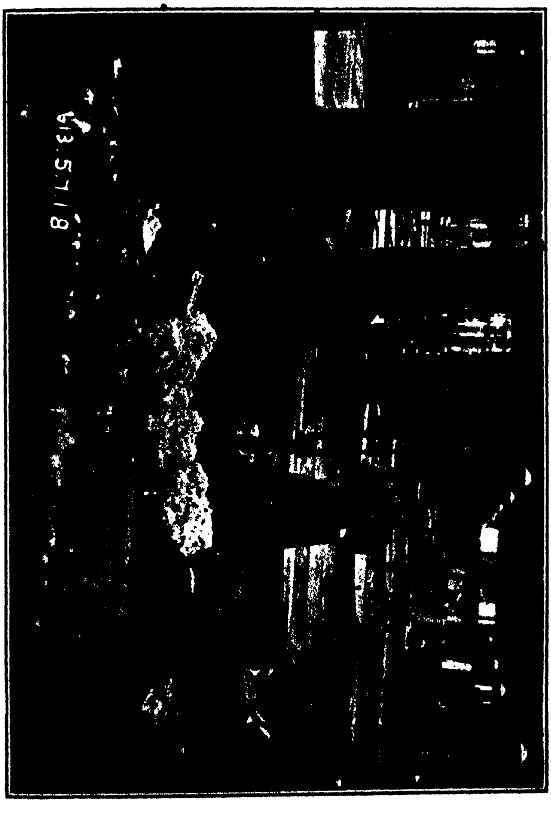

FIG. 276.—LOADING THE NITROCOTTON INTO THE PRELIMINARY BOILING TUBS

are indiscriminately selected from any of these, so that blending is carried out in the beaters.

Fineness. The fineness of the product is judged by the feel and inspection of the pulp in the hand, but in addition, a general sample is taken daily and sent to the laboratory for fineness and alkalinity determinations—the settled volume from 10 gm. in 200 cc. water being measured after 30 min. The reading aimed at is 100 cc. or less, and this figure should be obtained with a two-hours' total cycle, but is dependent upon the condition of the bedplate and roll in the machine.

Blanket Grit Separation. From the beaters the pulp flows to the stuff chests previously described, and thence over blanket launders, through grit traps, over long fiber combs, and magnetic separators to the poachers. The ratio of nitrocotton to water in these launders is approximately 1:20. The grit which is carried by the nitrocotton settles out on the blankets and in traps. Any long fiber which has missed cutting on the beaters is combed out by the long fiber trays, which consist of strips of wood with projecting screws and small particles of metallic iron which fail to settle on the blankets are held by the magnetic separators. After each eight beaters have been sent over the grit runs, the blankets are taken up and washed in a special tank provided. The tank is fitted with a series of scrapers, over which the blankets are drawn. The pulp is washed by decantation, the nitrocotton in suspension overflowing to the grit tanks. The residues are burned.

Poaching. Six beater charges constitute one poacher charge, this being known as a "batch," the weight being approximately one ton dry nitrocotton, giving a ratio of nitrocellulose to water of 1:15. Eight pounds of reprecipitated calcium carbonate are added. The machine is then filled with cold water, and the circulation pump started. The run is for 15 min., after which the circulation is stopped, the material allowed to subside for 20 min., and the process repeated. The charge is washed in this manner five times, the total quantity of water used in washing being 32,000 lbs. The decanting rate is 1500 lbs. per minute.

The last skimming is carried to 4″ from the surface of the pulp, and the circulating pump again started. A batch sample is then taken, and the charge directly pumped to the blender.

Blenders. Four poachers form a blender charge—termed a blend—is kept in the blender house until a sample, sent to the laboratory, has been passed upon. The batch samples are kept in the house until the blend analysis has been completed.

Re-worked Nitrocellulose. This is obtainable from the following three sources:

1. From the nitrocellulose drying stoves.
2. From the nitrocellulose screening house.
3. Incidental, in various steps of manufacture.

Drying Stoves. The nitrocotton for re-work from the drying stoves save-alls is delivered in tank cars to the pulping house, and from these is pumped by a 3″ pump into the re-work tank.

Screening House. The material from the nitrocellulose screening house save-all is pumped direct by means of a $2^1/_2$″ pump into the re-work tank in the pulping house. From the latter it runs over a special set of grit separation launders into a trough, from which it is pumped to a special poacher by means of a 3″ pump. In the poacher the nitrocellulose is given a batch number, washed as a normal charge and sampled, but without the addition of calcium carbonate. If the analysis is within specification, the charge is distributed over three blends. The blankets from these runs are washed in a special washing trough, from which the washings overflow into the save-all, while the residue is destroyed.

The nitrocotton from the main save-all is pumped directly into the switch box feeding the main grit separation launders, where it is blended in with process nitrocotton from the beaters. Re-work from the narrow save-all is pumped into the re-work tank, and thence sent to the switch box feeding the main grit separation launders. The long fiber nitrocellulose from the combs and other sources is picked over into a filling beater.

Short fiber re-work from the grit separation launders, and blanket washing troughs, is allowed to overflow from the troughs into the clean grit tanks, and thence is again pumped to the launders, where it is blended with normal process nitrocotton from the beaters.

Decantings from these troughs are run into the dirty grit tank, thence pumped across the main grit separation launders into the clean grit tank, from which it is again pumped over clean blankets into the poacher.

Pulping House Wringing. In the blender, the pulp is kept agitated until required, then the circulating pump is started and the pulp circulated round the pipe system behind the wringers. Valves are placed along the pipe line, one opposite each pair of centrifugal machines, and the pulp is drawn off as required into bags in the centrifugal machine. Time of spinning is 15 min. at 1100 r. p. m.; average moisture content, 31%; charge per machine, 0.055 ton.

The nitrocellulose is unloaded from the centrifugal machines into tared trucks which are wheeled on to a weigh bridge, and then despatched to the screening house.

Screening Nitrocellulose. The object of the screening process is to bring the nitrocellulose into a perfectly loose and uniformly fine condition before drying—another step in blending. The nitrocotton after it leaves the wringers is brought from the pulping house, the centrifugalization having reduced the moisture content to 31%–32%, and is put through the screening machines, which are of the nutmeg-grater type. The screened nitrocellulose is despatched in rubber bags to the drying stoves or to the magazines.

The screening house building is of iron, about 145′ x 50′, having an annex 18′ wide x 150′ long on one side. All floorings are of asphalt, and are in the so-called "clean" area, the main building having an upper and a lower floor. On the upper are located the 12 reciprocating screening machines, under which hang calico hoppers and bag holders 9 (refer to Fig. 273), which are attended to from the bottom floor. On the opposite side of the bottom floor to the annex is a loading platform where the screened nitrocellulose is loaded on trucks for despatch.

Between the pulping house and the screening building are located two electric hoists and a conveyor belt, which serve for the transference of nitrocellulose from the centrifugals to the screens.

The Screens may be divided, for the purposes of description, into three parts, as follows:

1. The reciprocating bin, with its flat, rectangular perforated cast iron plate bottom (or screen), all mounted on wooden wheels running in wooden grooves. The reciprocating motion is given

to this bin by means of a connecting rod actuated from an eccentric, which runs at 40 r. p. m.

2. Stationary baffles supported on a rigid framework. These serve to rub the nitrocellulose through the screen as the latter, full of nitrocotton, passes to and fro underneath the baffles.

3. Hoppers and bag holders under the screen, to facilitate loading the screened nitrocellulose into rubber bags on the bottom floor of the house.

The Reciprocating Bin or Screen consists of a rectangular wooden frame 8′ 10″ long x 5′ 2$^1/_2$″ wide x 6″ deep, inside dimensions, the thickness of the sides being 2$^1/_2$″, and of the ends 2″. This bin is strengthened by means of nine $^1/_2$″ bars, running longitudinally, and seven iron cross-bars 2″ deep and $^3/_8$″ wide. The frame, bars and cross-pieces all serve to support the screen, so that it cannot buckle under the pressure to which it is subjected. Attached to the top edges of the frame is the screen, the latter being made of punched, galvanized iron plate, in three parts, the joints of the parts being covered by 2″ thin iron strapping, which is screwed to 3″ x 2″ wooden cross-pieces underneath. The holes in the screen are $^3/_8$″ diam., and about one-third the circumference of each hole is raised into a lip which serves to slice off the nitrocellulose; as the lips wear down the efficiency of the screen diminishes correspondingly. The holes are spaced about 1″ centers, and the lips are arranged in the opposite direction in alternate rows. Thus, for each movement in one direction of the screen one-half of the total number of lips are cutting the nitrocellulose. The sides of the frame and screen project a foot past the end baffles. At one end is attached the connecting rod which moves the screen, the latter being supported on four hardwood wheels, each 10″ diam. and 2″ thick, and each made of a single piece of wood. The wheels have brass bushings, and rotate on iron spindles which are attached to the front girders. The spindles have each a grease cup at the end, and the lubricant passes through a hole in the spindle to the bearing. The screen frame carries four runners, each of which rests on one of the wheels. The periphery of each wheel is rounded, and each runner has a corresponding groove to suit, so that the frame is kept in position as it slides to and fro on the wheels.

Each runner is 1′ 9″ long x 6″ wide x 2″ deep, and is attached to the frame by a length of angle iron. Attached to the frame, and rising above the screen, is a wooden edging $^{7}/_{8}''$ thick, $13^{1}/_{4}''$ deep at the sides, and 9″ deep at the ends. This edging serves to prevent any unscreened cotton from getting into the hoppers. The screen makes about 40 reciprocations per minute, corresponding to 40 revolutions per minute of the eccentric on the machine shafting.

The screen holds at one time about 10 wringing bags, each containing 40 lbs. of wet nitrocellulose (31% water), or a load of 400 lbs. in all

Stationary Baffles. A rigid rectangular wooden frame made of 2″ lumber, 6′ $6^{1}/_{2}''$ long x 4′ $3^{3}/_{4}''$ wide x $11^{1}/_{2}''$ deep, inside dimensions, supports seven wooden baffles placed at right angles to the direction of the screen's motion and spaced equal distances apart. The baffles are 5″ deep and $1^{5}/_{8}''$ thick; each has a piece of 3-ply balata belting, 2″ deep, let into a groove on the under side. The bottom edge of each piece of balata just touches the surface of the moving screen and keeps the mass of cotton stationary in the bin, while the moving screen slices off particles from the under surface. The baffles are let into vertical slots in the sides of the stationary frame, so that when it is necessary to clean the machine all the baffles can readily be taken out. An opening 2″ high is cut along the bottom ends of the frame, thus preventing the cotton packing between the bottom of the frame and the screen. The frame is supported by four iron straps, 3″ x $^{1}/_{2}''$, which are bolted to the floor girders and stayed by four inclined iron straps 2″ x $^{1}/_{2}''$.

Bag Holders. The device for holding the rubber bag containers of the screened nitrocellulose consists of a round iron ring over which the top edge of the rubber bag is lapped. Supporting the bottom of the bag is a small-sized wood seat $2^{1}/_{2}'$ above floor level, hung from the iron ring. The iron rings are hung in pairs from vertical spindles, so that they are free to rotate horizontally. At the mouth of each calico hopper is one pair of such ring bag holders. An empty bag can thus be fixed ready while its neighboring bag is filling, and swung around immediately the full bag is removed.

Power System of Screening House. One running and one reserve—duplicates. 15 h. p. motors of squirrel cage type, running at 1500 revolutions on 420 volts 20 amps., and driving through (a) a reduction gear giving a reduction of 80 to 22, (b) main driving belt 5" wide from a pulley on reduction gear shaft 14" diam. and 8" wide, to a large pulley on the main shafting 3' 9" diam. and 6" wide.

Main Shafting. Main shafting is about 100' long x 2½" diam. Supported at intervals by self-aligning bearings—distance apart varying, but usually about 9–10'.

Final Drive. Final drive is from pulley on main shafting 12" diam. by a 3½" belt to fast and loose pulleys on the 2" machine shaft. Pulley, 38" diam. x 3½" wide. Thence by a crank of 6" eccentricity, giving a stroke to the machine of one foot; 40 complete reciprocations per minute.

Screening House Save-all. When hosing down the floors of the screening house all spilt nitrocelluloses is flushed into open drains which lead into a save-all, consisting of two settling troughs, either of which can be shut off for cleaning. The troughs are each 20' long x 3' wide x 2' 8" deep. At the save-all is a 4" Douglas pump driven by a 2½ h. p. motor, by means of which the nitrocellulose which has settled in the save-all can periodically be pumped out by a suction hose connection and forced along an iron pipe main to the re-work plant on the floor of the pulping house.

Method of Operation. The nitrocellulose leaves the wringers in linen bags, each containing 10 lbs. of wet nitrocellulose (31% moisture). As the nitrocellulose is taken over at the pulping house weigh-bridge, a checker records the number of bags and the blend number. The trolley containing the linen bags of nitrocellulose is then trucked on to the lift and up to the upper floor of the screening house, where the trolleys are taken from the lift, run over to the machines and unloaded as required. The trolley, when empty, is returned to the pulping house floor by the lift to be refilled. The nitrocellulose, when emptied into a machine, is compressed and lumpy, and has to be broken somewhat by hand into fairly small pieces so that it packs well down between the baffles on to the screen. The machine is fed so that the baffles are always covered and the nitrocellulose is kept level with the top of the bin.

Downstairs, where the screened and purified nitrocellulose is caught in bags the procedure is somewhat as follows: Empty bags are fixed on to the two sets of bag holders, and the ends of the two calico hoppers each tucked into a bag. When one bag is full the hopper opening is closed by gathering in the hand, and the bag holder is swung round so that the empty bag is under the hopper, which is then loosened into it. The full bag is detached, tied up and loaded on a trolley, and an empty bag fixed in its place.

When the trolley is full it is pushed on to the weigh-bridge and the weight recorded (the necessary arrangements for obtaining tare of trolley and empty bags are, of course, made); thence it is taken to the loading platform, on to which the bags are thrown ready to be loaded on to the trucks which will take them to the drying stoves or the wet nitrocellulose magazines. Each rubber bag contains roughly 30–35 lbs. nitrocellulose (wet). The floors of the screening house are continually being cleaned free from spilt nitrocellulose, and at the end of each shift the house is thoroughly hosed down.

Working Results, Efficiency. The waste has been found by experiment to amount to 0.16% of the nitrocellulose (dry weight) received from pulping house. This waste is caught in the save-all and sent back to the pulping house for re-work, and cannot be recognized as loss.

Screening Capacity of Machine. The machine screens on an average of 0.925 ton nitrocellulose (dry weight) an hour. To screen nitrocellulose required for 1000 tons R. D. B., five machines would have to be working most of the time.

Drying Nitrocellulose. From the screening house the nitrocotton is transported to the drying house, where the moisture, down to about 1%, is removed by means of the drying arrangement as developed by K. Quinan,[1] and patented by him in 1906. The apparatus is shown in section in Fig. 277, in detail in the photograph (Fig. 278), and the general arrangement of the dry house containing 11 dryers in Fig. 279. The principle of the apparatus is the drying of nitrocellulose in comparatively thin layers by the passage of hot air through the mass, the material being placed on a cheese-cloth in a tray as shown at *a*, having a perforated or reticulated bottom a^1, and this tray is placed within an air-distributing receptacle, *d*, having a false bottom, d^1. The tray *a* is closed in by a screen. *c*, fitting air-tight by virtue of a flannel or other covering at the sides; the bottom of this screen consists of a finely meshed silk bolting-cloth. Hot air from a main *e* passes through a valved pipe, *f*, into the vessel *d*. The material before removal after drying may be cooled by the expansion of a jet of compressed air supplied through a valve pipe, *k*. Separate drying units formed as above, may be set in alcoves *l* with fire-proof walls l^1 and open tops; the drying units will be supplied from a single hot-air main.

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[1] E. P. 22783, 1906; abst. C. A. 1907, **1**, 2034, 2054. J. S. C. I. 1907, **26**, 552; Zts. Schiess. Spreng. 1907, **2**, 277.

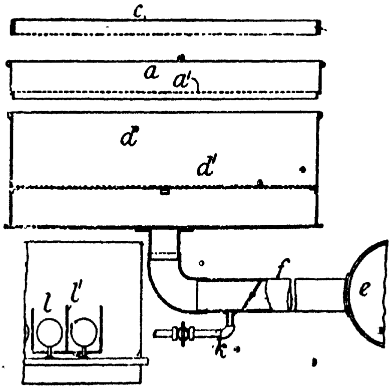


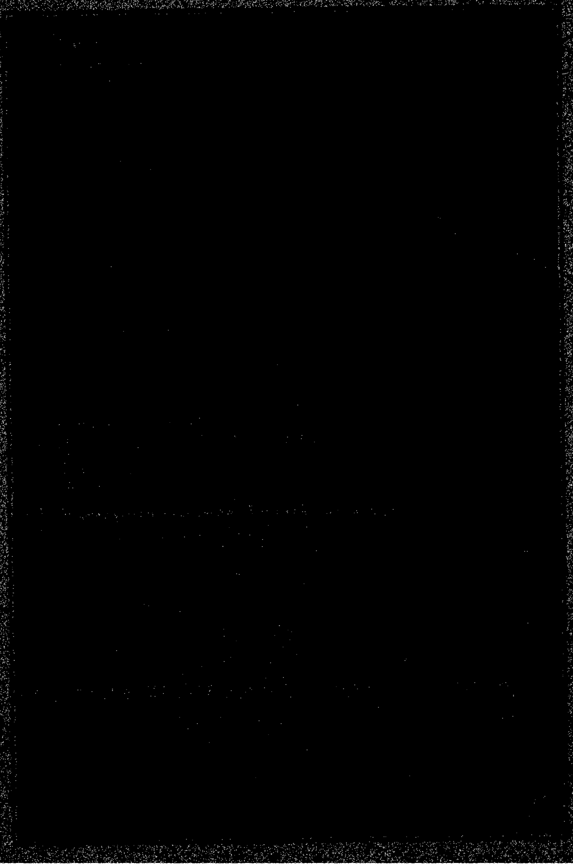
Fig 277.—Quinan Nitrocotton Dryer

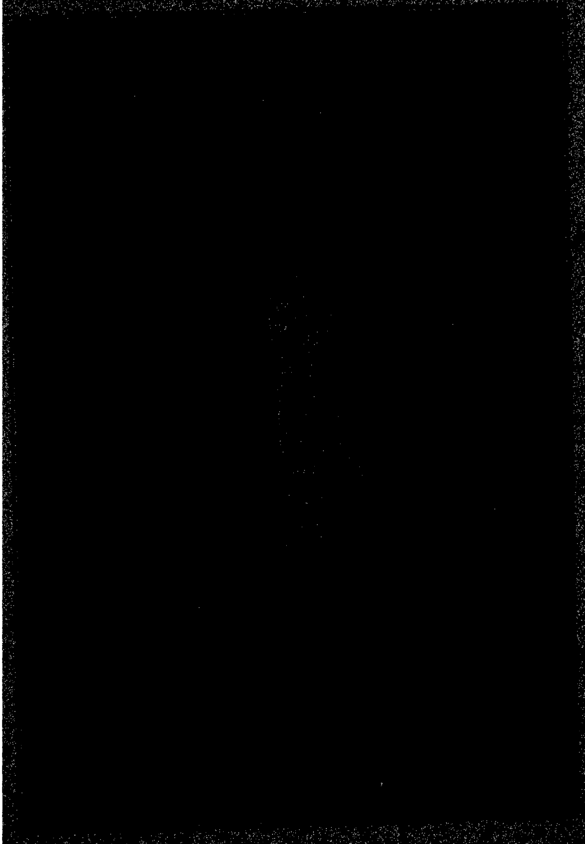
An amount of nitrocotton containing 31%-32% of water of such weight that, when dry, the weight will be 220 lbs. net dry, is dried to 1% moisture with cold air at 67°-68° F. for one hour. That is, the entire operation of loading the Quinan dryer, drying and removing the charge, consumes 60 minutes, of which 45 minutes constitutes the actual drying period. Three minutes is required to load the dryer, and after the water has been expelled, the dry nitrocotton is allowed to cool from 10-12 minutes before removal.

Description of Plant. There are 41 drying houses, or "stoves," as they are commonly miscalled, each spaced 200 feet apart for safety.

A unit consists of two stoves supplied with hot and cold air from one hot air apparatus house. There are therefore $20\frac{1}{2}$ units.

Each drying house is divided into a wet porch at one end, then the drying room and weighing room, and dry porch at the other end. The wet nitrocellulose thus enters by a 2′ track at one





end, and leaves, after being dried, by another 2′ track at the other end.

The drying houses are built in rows of ten, with the wet porches of one row facing the wet porches of another row. Thus one 2′ gauge main line serves two rows of houses. The same with the main tracks for the dry nitrocellulose.

The drying room of each house contains 15 round tinned sheet-iron drying pans 4′ diam. 16″ deep, open at the top and closed at the bottom, except for a 4″ air inlet pipe. A removable air-distributing plate is first put in the pan, consisting of a diaphragm punched with $^5/_{16}$″ diam. holes, $1^1/_2$″ centers. This diaphragm has a felt binding around its edges and another piece of felt is attached to the top edge of the pan. This precaution is necessary to avoid possibility of dangerous friction. Above the distributing plate is a removable circular tray or basket 4′ diameter and 4″ deep, having a copper gauze bottom.

The pans are all placed along one side of the drying room and separated from one another by a $4^1/_2$″ brick partition 8′ 6″ high and extending a distance of 6′ into the room.

The hot or cold air is turned on by means of cords projecting through holes in the brick wall of the building, and operating the air valves outside the building.

A drying house as a whole is 129′ long (over-all); 15′ broad (internal); 12′ 6″ high to ceiling, and is divided as follows:

Wet porch	9′ × 15′
Drying chamber	102′ × 15′
Weighing room	15′ square
Dry porch	15′ × 8′ 6″

Apparatus House. This is a brick building, 24′ x 16′, situated between each pair of stoves, which it supplies with both hot and cold air for drying and cooling, respectively.

Hot Air Supply. Air is taken through a rectangular opening placed high up in the eastern wall, and fitted with louvres to prevent the ingress of rain. Six feet west is the inlet of the Sturtevant heater, into which pass 150 cubic feet of cold air per second during normal running.

The heater is a rectangular box of sheet-iron about 13′ long x 4′ wide x 6′ high. The air first passes over a set of 16 steam coils, each coil consisting of a series of inverted U's, alternate coils being staggered, and all containing steam at 80–100 lbs. pressure—suitable control valves, gauge and traps being, of course, fitted. The air thus heated then passes through a filter at the exhaust end of the heater, the door for the removal of this filter also serving for the control of the temperature of the air supply, cold air being admitted as required. This filter consists of a series of wooden frames, covered with fine cotton bunting, which are set zigzag across the heater (concertina fashion) so as to give a very large filtration area, and is fine enough to stop not only dust, but also acid mist, which frequently contaminates the atmosphere. The filters have, therefore, to be regularly taken out and washed with alkaline solution.

From the filter the air passes to a Sturtevant fan, with an impeller about 2′ in diam. x 1′ wide, which delivers the air through a 28″ pipe, in which the temperature is noted, to the 20″ mains running from the back of the houses to the stoves. This fan is belt-driven at 1000 r. p. m. by a 15 h. p. squirrel cage motor.

Cold Air Supply. This is similar to the hot air supply, except, of course, the heater is omitted and the whole is smaller, as only a little cold air is required. The cold air Sturtevant fan has an impeller 1′ in diam. and 6″ wide, and delivers the air through the back wall to the cold air supply mains. The fan is belt-driven at 2000 r. p. m. by a $2^1/_2$ h. p. motor.

Drainage and Save-all. The floor of a stove slopes slightly from the side the pans are situated on, and terminates in a gutter running along the opposite wall. The outlet of this gutter is just inside the drying chamber near the wet porch and consists of a 4″ earthenware pipe which protrudes on the outside into a small sump. On this pipe a flannel bag is fixed, and is frequently changed, the waste being transferred to rubber bags which are periodically collected by a tractor-drawn truck and taken to the pulping house. The outlet from the sump leads into an uncovered drain. These branch drains all run in front of the wet ends of the stoves, and join a main drain which cuts across the area north and south. All sumps are asphalted, and the smaller drains are wooden asphalt-lined boxes along which the waste nitrocellulose passes easily. The main drain of asphalted brickwork leads into a central save-all. Asphalting is essential to prevent algae growth on the drains in summer, which later finds its way into the save-all and gives the recovered nitrocellulose an unworkably high ash content.

The save-all is situated on the south side of area. This is a brick-built structure, and divided into two troughs, which are concrete-lined, either of which may be shut off for cleaning. The water containing nitrocellulose in suspension comes in at one end of the trough; the nitrocellulose settles in the trough, and water passes on over a weir at the far end of the trough.

The dimensions of the trough are: 79′ long, 10′ broad, 3′ 6″ deep sloping to 4′ deep at the outlet end. Between the two troughs is a 2′ railway connected with the south dry track. The whole of the save-all is covered with a wooden roof.

A main steam line runs down the center dry track, and from this branch lines lead to the apparatus houses of all the rows. A reserve line runs down the south side of the area, and is used in case of emergency. The steam is at boiler pressure, about 145 lbs. per sq. in. up to a reducing valve on the branch line, after which it enters the apparatus house at not more than 100 lbs. per sq. in. The dimensions of the steam lines are as follows:

The main down center track	6″ tapering to 4″
Branch lines	3″ tapering to 2¼″
Reserve line	4″ all the way

Each stove derives its supply from six 1″ taps.

Bag Examination Room, where all empty paste bags from Cordite Area are carefully overhauled, is situated at the extreme west end of the nitroglycerol area on the dividing line between the nitroglycerol section and drying section. The building is brick with asphalt floor, which is kept as a clean area. On one side there is a loading platform, along the side of which the paste wagons arrive on standard gauge dry track with empty bags. On the opposite side is a narrow-gauge track where the dry trucks arrive for supplies of empty bags for the stoves. The building is provided with two small save-alls to catch the waste.

Sewing Room is a small building of wood, having asphalt floor which is kept as a clean area. In this room all sewing repairs are done. The work is mainly comprized of the following items:

Making and repairing of muslin sheets.
Making and repairing of grit screens.
Repairing of rubber bags.

Screen Cleaning Room is a small brick building where the air filter screens from the apparatus houses are washed and repaired. There is a motor-driven vacuum cleaning installation for use when the only cleaning required is the removal of dust.

Method of Operation of Drying Stoves. On arrival at the stove, the bags of wet nitrocellulose are placed in a space provided for that purpose in the drying chamber. The bags are then opened—the weight adjusted so that approximately 23 lbs. (dry weight) are contained in each bag. This weight is varied in each stove by a few pounds on either side, as no two stoves have exactly the same air supply. As the nitrocellulose contains about 32% moisture, the total load is about 33 lbs. per pan.

A muslin cloth of "Red Cross Calico," or cheese-cloth, about six feet square, is next thrown over the drying basket, and on this the nitrocellulose is carefully spread. When an even surface is obtained a silk grit screen, supported on a circular wood frame which just fits inside the basket, is gently pressed into position on the top. This avoids the nitrocellulose being blown about. The hot air blast is then turned on.

The drying is carried out at a temperature of 65° C. ±3°, controlled from the apparatus house. Each pan takes five cubic feet of air per second.

The operatives then pass on to the next pan.

When dry the hot air is shut off, and the cold air turned on and allowed to run for nine minutes to cool the nitrocellulose before handling. After shutting off the cold air the nitrocellulose is removed and passed through a hopper under which has previously been tied an empty paste bag.

The bag is then carried to the weighing room and the weight adjusted against a lead counterpoise, which weighs 33 lbs. 15 oz. The tare of a bag is approximately 2 lbs. 15 oz., giving a net weight of dry nitrocellulose of 31.0 lbs.

The bag is securely tied, wiped down and set aside either on the ledge or in a truck for despatch to the nitroglycerol section. The work in the drying chamber is carried on in cycles. The pans are loaded and unloaded in regular sequence from 1 to 15. The air supply in a stove has been adjusted so that each pan receives the same quantity of air. The load is so fixed that the time of drying and the time of cooling, plus three minutes to unload and reload, is one hour. This is normal factory operation.

The 15 pans are unloaded and loaded in 45 minutes, i. e., three minutes to each pan.

Each hour, therefore, the operatives have 15 minutes in which to clean down and have a short rest.

A record is kept of time of drying and time of cooling of each pan.

The cycle frequently lengthens for various reasons, such as increased percentage of moisture in the nitrocellulose and fall of temperature due to reduction of steam pressure or high winds; but, generally speaking, it is readily maintained.

Working Results of the Quinan Drying Houses. The average output for a stove per day is about 3.4 tons dry nitrocellulose of 1% moisture, but this varies slightly with the weather conditions.

The consumption of steam in the heaters of the apparatus houses is 2.433 lbs. per lb. of dry nitrocellulose produced. In addition to this, the steam consumption due to losses on the main amounts to 41–41.6 lbs. per hour. The waste nitrocellulose, which is sent to the pulping house for re-work, amounts to about 1.5% of the dry nitrocellulose produced. The total loss of nitrocellulose on the area is not over 0.2%, owing to the efficiency of the save-all arrangements.

Cleaning Out Waste Nitrocellulose from Save-all. One trough is cleaned at a time by decanting off the water with a suitable skimming arrangement, and digging out the deposited waste nitrocellulose by help of a bucket and small hand-crane. The dirty nitrocellulose from the save-all is sent in small tank cars for re-treatment at the pulping house.

Bag Examination Room. The empty paste bags arrive at the unloading platform in paste wagons. They are unloaded by help of wooden hand-trays and carried into the room. Each bag is checked against a counterpoise weighing 2 lbs. 15 ozs. Bags which will not pass this test are shaken out to get rid of any paste they may contain. All bags are carefully examined as to soundness, etc., and are wiped down on the outside with a wet sponge. They are made up in bundles of ten, and to each ten a label is tied, on which is the name of the operative who examined the bags and the name of the chargewoman who checks the weight of each bundle, both as it arrives and is given out.

By this means careless work is easily detected. A bag is worn out and will leak paste when a brown ring appears around the bottom of the bag. Rejects are set aside and washed free from explosives, and are sent for repair or to the burning ground, according to the degree of damage.

Wet Nitrocellulose Magazines. *General Outline.* Three in number, situated to the north of the screening house, and about 70 yards away. The object of these magazines is to carry a stock of wet nitrocellulose which will ensure a constant supply to the drying stoves even in the case of a serious breakdown in the manufacturing plants.

Description of Plant. The magazines are brick built, and have an asphalt floor; each is 159′ long and 45′ broad. The space between each is 33′. They run lengthways north and south, with the only entrance at the south end. The floors are kept as clean areas, and are divided into twelve sections, marked off in white lines. The dimensions of one section are 22′ 4$^1/_2$″ x 19′ 11″, and the capacity is a little over 1000 bags, stacked nine high. Steam heating is laid on to prevent the nitrocellulose from freezing in winter.

Method of Operation. The stock of nitrocellulose is usually kept at the maximum capacity of the magazines, viz., about 300 tons (dry weight), and this is turned over at the rate of 900 bags or 7$^1/_2$ tons a day, which means that the whole is turned over in six weeks, thus preventing the nitrocellulose getting mouldy

Transportation of Wet and Dry Nitrocellulose. Trucking. From the loading platform at screening house a two-foot gauge railway leads to all the drying stoves and the wet magazines. The trucks used are tub-shaped, the internal dimensions being 8′ long, 4′ 1$^1/_2$″ wide, 3′ 10$^1/_2$″ high, and hold 30 bags of nitrocellulose. They are fitted with roller-bearings to provide easy running. Small fireless locos are provided for hauling the trucks.

Fireless Locomotives. The lagged boilers of the "locos" are charged with steam as 125 lbs. pressure in a shed close to the screening house loading platform. The steam for charging is taken off a steam main coming from the boiler plant.

Steam Consumption. Roughly 280 lbs. per 24 trucks of 30 bags each, the average haul of the loaded trucks being about 1400 feet. This works out to 42.5 lbs. of steam per ton of wet nitrocellulose trucked, figured on the dry weight of the nitrocellulose.

Trucking. Varying number of trucks, generally from three to six are taken from the screening house on one journey, which on arriving at the stoves are uncoupled at the side track leading to those requiring nitrocellulose. Men are on hand at the stoves to take charge of the trucks as they are uncoupled, and push them into the stove and unload them.

Empty bags which the men have collected while waiting for the train are taken back to the screening house on the return journey. Clean area boxes are placed at intervals along the track, into which these bags are placed until the train picks them up.

The distribution of wet nitrocellulose among the stoves is regulated by the checker, who is also weighing nitrocellulose in the screening house, who is guided by the mealtime and end of shift reports of stock sent in from the stoves.

Dry Trucking System. As the maximum amount of dry nitrocellulose allowable in any one stove is 18 bags (approximately 560 lbs.) and each stove can, under favorable conditions, dry this amount in one and a half hours, this is the greatest permissible interval between removals of dry cotton. The nitrocellulose is removed by a $2^3/_4$ h. p. electric tractor, which pulls the trucks in trains, which must, however, not exceed four trucks. The stoves served by one tractor in any one row on one line are, therefore, kept below eight in number, and the procedure is as follows: A truck is put into the dry porch of each stove, and the girls in the stove load this as their work proceeds. At a certain definite time (as laid down for their guidance in a carefully drawn-up time-table) two girls with the tractor start at the most distant stove of the row, and pick up trucks from every alternate stove, remove these to the exchange at the entrance of the nitroglycerol area, and return with trucks (either empty or once per shift normally, containing empty paste bags), which they place in the previously emptied stoves. Three-quarters of an hour after they started at the farthest stove they start at the next one and repeat the process, thus emptying every stove not previously visited, and completing the cycle in approximately an hour and a half,

the stoves thus never exceeding their limit of dry nitrocellulose. During the mealtime one girl carries on the work without any great difficulty, the amount of manual labor being so slight owing to the use of the tractor; though, on account of the limit on the number of trucks per train, eight stoves is the normal maximum per tractor. It is probable that three tractors could deal with the output from the 25 stoves necessary for an output of 1000 tons R. D. B. cordite.

The tractors are run by 100-120 volt accumulators of the iron-clad pattern, which require recharging about once every 24 hours, when the tractors are being used for eight stoves as described above—unless very carefully handled, when they will run for a few hours longer, their capacity being 120 amp. hours. They are refilled with newly charged spare accumulators so as not to delay the work, and the exhausted ones recharged in a converter station on the area, which is fitted with two duplicate 9.6 kilowatt converter sets, and the necessary electrical apparatus to deal with five tractors as two others are in use, one for trucking in the nitroglycerol area and the other for the collection of waste. Two types of dry trucks are in use, both of the roofed pattern, the sides being closed with tarpaulins secured with ropes. One type is 7′ 3″ long, 3′ 4″ wide x 6′ 3″ high. The more satisfactory type is 9′ long x 3′ 5″ wide x 5′ high. These latter are not so much affected by high winds so frequently in evidence. All are fitted with spring buffers to minimize the danger due to shocks, and fitted with roller bearings to provide easy running.

The pulped, screened and dried nitrocellulose is then in condition for incorporation with nitroglycerol and mineral jelly for the manufacture of cordite, details of the various steps from this point being a separate topic under the general topic "Cordite," in Volume VII of this series. The various steps in the entire process as carried out at Gretna are shown in Fig. 280 from the original cotton bale to the colloiding of the finished product for fabrication into cordite.

Labor Requirements. For an output of 250 long tons of nitrocellulose per 6-day week, the following are the labor requirements:

Cotton preparation department, 54 women. Nitrating house, 4 men, 240 women. Boiling house, 108 women. Pulping house, 6 men, 183 women, making a total of 10 men and 585 women.

In the cotton waste preparation, three units are run, requiring a general foreman, 2 chargewomen and 25 process workers; the latter being subdivided into 3 for bale breaking, 2 teasing, 13 drying, weighing and bin-running, 2 cooling, 1 cleaning and re-working, and 1 mechanic. In addition, 3 process workers on the day shift are required, carting bales from the bale store to bale breakers.

In the displacement nitration, 1 foreman, 1 chargewoman, 1 forewoman, 6 chargewomen and 74 process workers constitute the force. This is divided into 35 for dipping cotton waste, 14 unloading nitrocotton, 7 displacing, 7 trucking cotton waste, 6 trucking nitrocotton, 3 cleaning, and 2 plumbing. Each shift is under a working chargewoman. In dipping, a gang consists of 5 process workers, each one of whom runs up acid in turn. The five thus turn out 26 sets of nitrations per 7 hours.

In the boiling of the nitrocellulose, there is required 1 each, foreman and forewoman, 2 chargewomen, 4 for boiling and 30 process workers, the latter being subdivided into 7 charging, 20 discharging and 3 cleaning. The labor in this section is divided into two separate gangs, charging and discharging, each under its own supervisor, and distinguished by colored armlets.

In the pulping, poaching and wringing sections, one each, foreman, forewoman and chargeman, with one male process worker, 56 female process workers and 5 chargewomen, constitute the force. The 56 are divided into: 4 each bucket running and poaching, 5 grit separation, 8 wringing, 6 recovery, 3 trucking and weighing, and 2 mechanics.

Acids. The mixed acid is supplied in blends of 150–180 tons of a definite composition. The spent acid is issued in consignments of up to 150 tons, after passing through a continuous sampler. One sample is taken for each consignment, and the composition of the sample is taken as the composition of the consignment. A routine sample is taken on each shift of the drain waters leaving the buildings. On this sample the specific gravity, percentage of sulfuric acid and nitric acid are determined.

Boiling. The main supply water should be titrated daily, and the amount of sodium bicarbonate necessary to bring the total alkalinity to approximately 14 parts per 100,000 calcium carbonate, is calculated and added to the mixing tank. In the vat house samples of the water in use are taken hourly from a continuous sampling device, and titrated for total alkalinity. A sample of the liquor is taken after each boil and titrated for total acidity. After the second to the fourth boils samples are taken and their reaction tested with methyl orange. After the fifth boil the sample is tested with a solution of potassium iodate, potassium iodide and starch.

Nitrocotton Tests. A routine sample is daily taken from the vats which have finished process during the previous 24 hours, for the heat test. A routine sample is also taken from the beaters, and sent forward for fineness and alkalinity by each shift. A routine sample is withdrawn from the poachers, and the fineness, alkalinity and heat test determined. Individual samples are withdrawn from each finished poacher, before pumping to the blending tanks. After 30 min. agitation the blend sample is taken and forwarded to the laboratory for complete analysis. The individual samples are retained on the plant until the blend analysis has been completed. If the blend is within specification the individual poacher samples are mixed. For the purpose of issue, each blend is kept separate. A sample is taken from each sixth bag from the wringers and put into a sealed box. When the blend is complete these samples are well mixed and duplicate samples taken, one determined for moisture and the other retained for possible reference. To check this result every 20 minutes a sample is withdrawn from two or three bags of screened nitrocotton, mixed in a rubber bag, and the moisture determined.

Efficiencies. The consumption of cotton waste is approximately 0.67 ton gross per ton nitrocellulose produced, giving a yield of 161.5% net, of 12.15% nitrogen. The consumption of sulfuric acid and nitric acid to produce a nitrocotton of the above nitrogen content is 0.13 ton and 0.65 ton, respectively, per ton of nitrocotton produced.

Water, Steam, Power. The water consumption is approximately 165 tons per ton nitrocellulose produced, of which quantity 76 tons are used in stabilization by boiling, and 60 tons in beating and poaching. The steam consumption is 18 tons, and the power consumption 620 kilowatt hours, respectively, per ton of nitrocotton produced, but subject to slight variation.

Specifications for Nitrocellulose. The specifications for nitrocellulose as produced above are as follows:

1. The nitrocellulose must be free from unconverted cotton and free from all matter not permitted by the specification.

The nitrocellulose must be free from grit and should contain no other mineral matter than naturally present in cotton or taken up from the wash water and such as may unavoidably have been taken up from the machinery employed in the manufacture.

2. The total amount of mineral matter contained in the nitrocellulose is not to exceed 1%.

3. The percentage of nitrogen is to be calculated on the nitrocellulose free from mineral matter and is not to be less than 12.1% nor more than 12.3%.

4. The nitrocellulose to be at least 95% soluble in a mixture of 2 parts by volume of ether, sp. gr. 0.72, and 1 part of not denatured alcohol, 92% by weight.

5. The nitrocellulose when subjected to the Will test should disengage from 2.5 gm. not more than 6 mgm. of nitrogen in 4 hours.

6. The total sulfate present, calculated as H_2SO_4 on the dry nitrocellulose, must not be more than 0.1%.

7. The nitrocellulose must contain from 0.2% to 0.4% of calcium carbonate, calculated on the dry material.

Gretna Nitrocotton Manufacture Flow Sheet. The following results expressed in per cents and long tons (2240 lbs.), show graphically the detailed costs and yields in the various steps of manufacture, purification and rejuvenation, as carried out at H. M. Explosives Plant, Gretna, for a consecutive five weeks' period during the summer of 1918, all nitrogen acids being shown as HNO_3.

The total nitrocotton made was 1043.18 tons, requiring cotton waste, 710.28 gross tons, or 651.58 net tons, and 20928.2 tons mixed nitrating acid containing: sulfuric acid, 13004.5 tons (62.14%); nitric acid, 4915.4 tons (23.01%), and water, 3109.3 tons (14.85%); total acid 20928.2 tons (100%).

The spent acid recovered was 21011.7 tons, divided as follows:

1. Spent acid to be revivified. Sulfuric, 7344.5 tons (61.06%); nitric, 2366.3 tons (19.37%); water, 2317.9 tons (19.27%); total 12028.7 tons (100%).

2. Spent acid to be distilled. Sulfuric, 5493.6 tons (61.15%);

nitric, 1773.0 (19.74%); water, 1716.4 tons (19.11%); total 8983.0 tons (100%).

3. Total spent acid. Sulfuric, 12838.1 tons (61.10%); nitric, 4139.3 tons (19.70%); water, 4034.3 tons (19.20%); total, 21011.7 tons (100%).

The total nitric acid consumed was 737.8 tons, accounted for by 676.1 tons consumed in nitration, to which is added a 3.48% loss on 1773.0 tons HNO_3 in the spent acid to be distilled, or 61.7 tons, giving a total of 737.8 tons.

The sodium nitrate used was 1086.0 tons crude, equal to 1042.5 tons $NaNO_3$, of which there were charged into the retorts (sufficient to produce 737.8 tons HNO_3) 986.4 tons; to which amount is to be added loss in nitration (difference between sulfuric in mixed and spent acids) 166.4 tons; then add 1.05% loss in concentration of 5453.5 tons weak sulfuric from stills, or 57.3 tons; then add 1.05% loss in concentration of 142.6 tons weak acid from oleum plant; then add 0.73% loss at stills on 5493.6 tons used to distil weak nitric acid, or 40.1 tons; thus giving a total consumption of 1251.7 tons. The SO_3 consumed was 1021.8 tons.

The sulfur consumed in the Grillo plant was 446.4 tons. The sulfur charged in the Grillo was 832.25 tons (96.18%), which produced 1904.8 tons, SO_3, or a 95.2% efficiency. Therefore, 1 ton SO_3 required 0.4369 ton crude sulfur, and 1021.8 tons SO_3 required 446.4 tons crude sulfur as above stated.

In calculating the acid to be distilled, the nitrocotton spent acid amounted to 8983.0 tons. There were charged into the stills 9127.6 tons spent acid of composition, H_2SO_4, [illegible].3 tons (61.15%); HNO_3, 1801.5 tons (19.73%), of which were recovered of the above two acids, 5540.4 and 1738.8 tons, respectively; the loss, therefore, was, sulfuric, 40.9 tons (0.75%); nitric, 62.7 tons (3.48%).

The nitrocellulose spent acids to be distilled (8983.0 tons) comprized sulfuric, 5493.6 tons (61.15%); nitric, 1773.0 tons (19.74%). The sulfuric to be delivered to the concentrators was: from the nitrocotton spent acid, 5493.6 tons; less loss (0.73%), 40.1 tons, or 5453.5 tons.

The calculations involved in the acid to be fed to the concentrators as sulfuric, totaled 5596.1 tons; and to be delivered *from* the concentrators as H_2SO_4, 5537.3 tons. The Gaillard towers working during the period required for charging 9441.4 tons (76.94% H_2SO_4), from which were recovered 7729.6 tons (92.99% H_2SO_4), a loss of 76.7 tons sulfuric acid. The sulfuric lost, therefore, was 1.05%. The loss in weak acid from the stills was 5453.5 tons; proportion of weak acid 'ex oleum plant,' 142.6 tons; total, 5596.1 tons. From this is subtracted the loss of 1.05%, or 58.8 tons recovered from the concentrators, giving a total of 5537.3 tons.

Taking the above figures, and calculating them on the basis of requirements for the production of one ton of nitrocotton, we have: cotton waste used, gross tons, 0.681, or net tons, 0.624, requiring 20.062 tons of mixed acid, of the composition sulfuric, 62.14% (12.466 tons); nitric, 23.01% (4.616 tons); and water, 14.85% (2.980 tons); total, 20.062 tons (100%).

The spent acid was 20.142 tons, of which 11.531 tons were to be re-fortified. This was composed of, sulfuric, 61.06% (7.041 tons); nitric, 19.67% (2.268 tons); and water, 19.27% (2.222 tons); total, 100% (11.551 tons). There was also to be distilled, 8.611 tons, composed of sulfuric, 61.15% (5.266 tons); nitric, 19.74% (1.700 tons); and water, 19.11% (1.645 tons). There was thus consumed in nitration, 0.648 ton, to which is added 0.059 ton loss at stills, giving a total of 0.707 ton. 1.041 tons of sodium nitrate were employed, equivalent to 0.999 ton $NaNO_3$. The sulfuric consumed at the retorts figured 0.946 ton; loss in nitration, 0.159 ton; loss at stills, 0.039 ton; loss in concentration, 0.056 ton. Total, 1.2 tons. The SO_3 consumed was 0.979 ton, and the sulfur, 0.428 ton.

The nitrocotton spent acids formed was 8.6111 tons. The acid to be fed to the concentrators as H_2SO_4, 5.364 tons; while the acid to be delivered *from* as H_2SO_4, was 5.308 tons.

Guncotton Manufacture at Queen's Ferry Plant.[9] The manufacture of nitrocellulose at the Queen's Ferry plant differs in one very important particular from the nitrocotton produced at Gretna, as previously described. Whereas at Gretna a so-called pyrocollodion nitrocellulose is produced of nitrogen content around 12.2%, and a solubility of around 95% in ether-alcohol, at Queen's Ferry a straight guncotton is manufactured of nitrogen content of 13.0%-13.15%, and an ether-alcohol solubility of but 6%-8%. The following details of manufacture, therefore, where they differ from the prescribed Gretna practice, are for the production of this high nitrogen per cent. nitrocellulose, which is colloided with acetone for the production of smokeless powders of the cordite type, which require nitroglycerol in conjunction with the cellulose nitrate. The details of this process to be described, may be taken as fairly illustrative of the most advanced methods of high nitrogen cotton nitration as practiced in Great Britain at the present time.

The preparation of the cotton suitable for nitration from the crude cotton waste is conducted along the same general principles as followed at Gretna, and as previously outlined (see p. 2188), variations in treatment being primarily along mechanical lines. The cotton after passing the requisite tests for appropriateness for esterification, is allowed to stand at least four hours (preferably six hours) after the final drying process, in order to permit of the cotton regaining ordinary room temperature, but during this time protected from the atmosphere in order to guard against the absorption of atmospheric moisture. The plant was originally laid out for a production of 100 long tons of guncotton per 6-day week. The purified warm cotton is transferred to air-tight tins, stacked several high owing to limited accommodation of the cooling room, this work, as well as the major portion of the work at this plant, being performed by girls.

The nitrating plant consists of 11 rows of 13 sets of 4 Thomson displacement stoneware pans, 3′ 8½″–3′ 9″ diam. x 11″–11½″ deep (at the circumference), each set of four pans being served with acid from an iron main through an 1½″ inlet cock; the displaced (spent) acid being run off to the strong or weak acid main through ¾″ 3-way cocks and a lead siphon tube. To preserve the desired rate of flow, it has been found necessary to throttle the acid back with a glass tube 9.5 mm. diam. and 1½″ long, this giving a total displacement in about three hours. In the sight glass (1″ diam.) is a float bobbin which sinks in liquid of less than 1.2 sp. gr., while the level of the acid in the sight glass to be maintained during the displacement is marked by a painted line or rubber band.

Water distributors of the ordinary type are used, rubber tubing and aluminium troughs being employed to direct the water on to the pans, although the former are more serviceable, enabling he overflow of the pans during displacement to be stopped, thus ending to keep the floor more or less dry.

Draught is obtained by means of 8 sirocco fans, arranged in four batches of 2, one for use and one for spare. Each pair serves one quarter of the nitrating house, the fans being direct coupled to 7.5 h. p. motors, at 570 r. p. m. On the assumption that ten out of the eleven rows are continually in working order, with a pan cycle of 7 hours, 26 lbs. of cotton per pan, and a yield of guncotton of 1.65, on a 24-hour working day, the weekly capacity of the nitrating plant would be 239 tons of guncotton.

The acid storage tanks are dipped (tested as to capacity) each morning, and also during the day before and after pumping from or into a tank, the mixed acid used and the spent acids produced being thus ascertained. The acid is run into a set of pans, one set ahead of the cotton dipping operatives, the level of the acid in the nitrating pan determined by means of an aluminium gauge about 3″ long on the side of the pan, the temperature of the incoming acid regulated, and the fume hoods put in place.

Each shift of dippers has a row and a half allotted to it, and when the dipping of 20 sets of pans has been accomplished, the work is said to constitute a day, and the workers are allowed to leave the building. A small curved aluminium or iron tray is hung from the front of the pan to prevent the cotton waste from being spilled on the floor, aluminium pokers being used for laying the sector plates on the nitrated cotton in the displacement pan, and to poke the projecting pieces of cotton under the nitrating acid. The dipping forks are of aluminium head, with four prongs and a steel shaft. The workers stop the acid from running along the handle to the hands by means of a piece of cotton waste or rubber disc fastened on to the handle.

The guncotton from one row of pans (13 sets, or approximately one ton of nitrocellulose) is loaded into one vat. For a weekly output of 100 tons, there is required 6 rows of pans, which necessitates the filling of 4 vats at the same time.

When the series of nitration was commenced, the nitrating mixture comprized 71% sulfuric acid, 21.5% nitric acid, and 7.5% water. When the manufacturing process had been placed on a permanent normal basis, the mixed acid composition was maintained at: sulfuric acid, 69.5%–70.3%; nitric acid, 20.8%–21.3%

and water, plus nitrous acid, 8.5%–9.5%. This gave a nitrogen of 13%–13.15% in the nitrocotton produced and an ether-alcohol solubility of 6%–8%. A rise in solubility to 12% was observed when attempts to economize acid were made, the ratio total of mixed acid used to cotton being 32–33.5, assuming the cotton to contain 0.5% moisture. On increasing this ratio to 34–35, the solubility dropped to 7%. The bottom plates of a pan displace about 134 lbs. mixed acid of the composition as above stated. Other acid unavailable for nitration is 9.8 lbs. in the lead pipes, and 38.2 lbs. below the bottom plates, a total of 48 lbs. The total mixed acid per pan for a ratio of 1:34.5 charge of 26 lbs. cotton was 897 lbs., less 48 lbs. as above, or a net available amount of 849 lbs. thus giving a ratio of available mixed acid to cotton of 1–32.65. The ratio of total mixed acid to cotton of 34, gives a ratio available of mixed acid to cotton of 32.15. A 26-lb. charge was used for the production of guncotton, and a 27.25-lb. charge of cotton for a nitrocellulose of solubility similar to that previously described as produced by the similar process at Gretna.

After the nitration process has been completed, the acid is displaced by means of cold water, the acid run to strong spent acid for 2 hours 20 minutes, and this gives a percentage of strong spent acid of the total spent acid of 75%–78%. The time of nitration was $2^1/_2$ hours. Average analyses of products over a fortnight period were:

	H_2SO_4	HNO_3	HNO_2	H_2O
Strong spent acid ...	71.64%	17.59%	0.49%	10.28%
Weak spent acid ...	63.70%	17.27%	0.42%	18.61%

the proportion of mixed acid used being about 34 to 1 of cotton waste. The acid is turned to drain at about 1.2 sp. gr., as shown by the fall in the float.

In the vat boiling room the vats are 9′ 6″ diam. at top, 10′ at bottom, and 7′ $2^1/_2$″ over all in height. The bottom slopes from 6′ $1^1/_2$″ deep to 6′ $7^1/_2$″ deep, with a false bottom 2″ thick on bearers 3″ x 4″. The volume of water required for displacement is 3200 gallons, which is approximately the capacity of the vat. All displaced water is led away to the surface drain through earthenware pipes. The water is supplied from two batteries of 3 tanks, each 21′ diam. x 10′ 6″ deep, thence through constant level tanks feeding the aluminium launders in the vat room. Due to the alkalinity of the water supply used (the Halkyn water having an alkalinity equivalent to 18 parts per 100,000), no soda was used in boiling. Otherwise, the vat boiling operation is conducted substantially as previously described.

Pulping. At Queen's Ferry the pulping is divided into the following five units: a. Pulping (beating). b. Poaching. c. Pressing. d. Magazines. e. Box stores.

The pulping plant consists of 11 Bertram beaters 12′ x 6′, 200 r. p. m. = 1924 f. p. m. peripheral speed, roll 42″ diam., driven by 40 h. p. alternating current motor, 440 volt, at 480 r. p. m., and 12 Bentley & Jackson beaters, five of 15′ x 7′ driven by 50 h. p., and seven of 14′ x 7′ alternating current motors, at 160–180 r. p. m., with a 4′ 3″ diam. roll = 2410 f. p. m. peripheral speed. Each type discharges into an aluminium launder under the stage leading to two stuff chests, from which the pulp is pumped to the grit runs.

Grit Runs. Two series of 4 runs ending in magnets, magnetized by 100-volt direct current, are provided. The pulp is then led into the launder leading to the poachers, or alternatively to grit tanks below, for further circulation over the grit runs. The capacity of the large beaters is 640 lbs. guncotton per charge, and of the smaller, 320 lbs. guncotton, the average cycle of the two sizes of beaters being $3^1/_2$ and $2^1/_2$ hours, respectively, the charge per beater per 144-hour week being 141 and 91 tons. The capacity of any beater can be materially raised if constant supervision is made as to the state of the shoes and rolls, and the method of operation. The guncotton is slowly fed into the beaters by hand, this process occupying 30-45 min., close watch being kept for the introduction of impurities, especially splinters of wood. The charge must be kept in constant agitation with aluminium paddles, especially when the pulp becomes finer. The bulk of water should be kept at a minimum.

After beating to the required fineness the plug in the beater is withdrawn and charges from two beaters are run into a launder below, and led to one of two stuff chests, from which it is pumped over grit runs. These latter have blanketing laid down, held in position by lead straps. The wells, which are placed at intervals down the run, serve to retain grit and heavy particles.

At the end of the run the pulp flows over two magnets into a box connected with the launder feeding the poachers. At the end of the four grit runs at each side of the building is an aluminium box divided into two sections, from each of which the pulp flows over two magnets.

After each half-ton charge and one grit charge, the blankets are removed and washed in a blanket tank 2′ 3″ wide x 7′ long x 16″ deep, having a wooden partition 2′ 3″ from one end and 13″ high, on the top of which is an aluminium plate with $^{1}/_{4}$″ holes.

Poachers. The plant contains 15 of these machines, 12′ wide, 24′ long and 3′ 1″ deep, inside measurements. The charge is circulated by an impeller pump at 440 r. p. m., driven by a 250 h. p. alternating current motor, 440 volts, 480 r. p. m. The run-off pipe leads to the impeller pump, and the discharging pump to the blender tanks. Each poacher holds with ease a ton charge of nitrocotton, the cycle of a poacher being: 5 washings of $^{1}/_{2}$ hour each; 6 skimmings of $^{1}/_{2}$ hour each (15 min. settling and 15 min. skimming); washing with chalk, $^{1}/_{2}$ hour; and filling, $1^{1}/_{2}$ hours, a total of $7^{1}/_{2}$ hours, thus giving 3 poacher charges per day, or 45 tons capacity for the 15 poachers. After the addition of the chalk by straining through muslin an elutriated suspension, and then circulating the charge for 15 min., the contents of the poachers are pumped to overhead blending, tank feeding presses, by pump direct-coupled to 25 h. p. motor at 480 r. p. m. Assuming 4 lbs. of guncotton per cu. ft. water, the pulpers have a capacity of 340 lbs. guncotton per charge for the smaller pulpers and 548 lbs. for the larger. The poacher dimensions are 3′ 1″ mean depth, 2′ 4″ mean working depth, over-all inside width 12′, and over-all inside length 24′, giving a total working capacity of 426 cu. ft. The blending tanks are 21′ diam. x 6′ 6″ high, capacity 2250 cu. ft. The stuff chest for the pulper feed is 7′ diam. x 6′ high, capacity 230 cu. ft. The vacuum chambers are 6′ 6″ diam. x 6′ working height, capacity 200 cu. ft.

The following thirty points in connection with the working of a guncotton plant are of special reference to the machinery installed and methods of manipulation evolved as carried out at Queen's Ferry.

1. Before starting the beaters, see that the roll is lifted clear of the bed plate, the latter being the stationary box of knives in the bottom of the

trough immediately under the roll. Otherwise the beater knives may jam.

2. First, run water into the beater, and as soon as it is in circulation, feed by hand the nitrocotton into the water. The cotton and water, therefore, are fed into the beater together, until the required charge has been put in

3. After filling the beater with water and nitrocellulose, the roll is gradually lowered so that in 15–20 minutes after the full charge has been put in, the roll is lowered on to the bedplate to take nearly the full load of the motor without stopping it.

4. The pulp should be occasionally stirred with a paddle by hand to insure a homogeneous suspension, and to prevent settling at any point.

5. The time required to comminute a charge to the desired degree of fineness will primarily depend upon the efficiency of the attendant, the main factors being making the roll cut as hard as possible, which is determined by the power taken and keeping up a uniform circulation.

6. Care should be taken to see that the valves are not lifted out with the paddle while assisting circulation, and that the roll bearings are well supplied with lubricant.

7. In the manipulation of the stuff chests, care must be exercised that the agitators are not stopped while the chests are full of pulp, if possible, as the nitrocotton settles, and causes difficulty in starting.

8. The cock on the discharge branch of the centrifugal pump chests are regulated to give the desired quantity of pulp to the sand catcher chutes, as power is saved by so doing.

9. The plug valves in the bottom of the sand catcher chutes and in the inlet and outlet boxes must be lifted when washing out, to allow the waste pulp and sand to flow into the drain pipe, two by-pass pipes being provided to allow of deflecting the pulp from its course to the dirty cotton tanks, should this be found necessary.

10. The failure of the magnets, due to interruption of the current, will automatically by-pass the pulp into the sand gutter and thence into the dirty cotton tanks, until the current is restored; a signal bell apprizing the operator of such interruption.

11. When the pulp is circulating, the skimmer should be placed on the clips at the side of the potcher, being released when the potcher pump is stopped, and so adjusted that the surface water will drain away slowly, the floats automatically sinking as the level of the water falls.

12. Two pumps for emptying the potchers are provided, one acting as a reserve in case of any emergency, the pumps being connected by means of a flap valve so that the pulp can be deflected to either.

13. The six-inch discharge valve of each pump should be throttled down so that the pump will throw the desired quantity of pulp, to avoid unnecessary consumption of power.

14. Running pulp into the pumps prior to starting will cause difficulties, which can be remedied by closing the discharge valve until the pump is started, and then gradually opening the valve to the desired point.

15. A three-way cock is provided on the discharge branch of one of

the pumps to act as a washout for all the pulp piping under the potchers.

16. Three cocks are provided so that the pulp can be delivered into any one of the blending tanks.

17. The plug valve fitted in the outlet from the bottom of each tank should be closed before the six-inch cock on the underside is closed, so as to prevent pulp from lying in the short piece of pipe between the cock and the plug valve; a hand lever being provided to operate these from the top platform.

18. The stirrers in the blending tanks should not be stopped when there is any pulp in the tanks, as this will cause difficulty in starting up again, due to settling out of the pulp. If any of the blending tanks are out of service, all cocks cutting off idle pipes should be closed to prevent the nitrocotton from packing in these pipes.

19. When starting up the vacuum pump the three-way cock on the suction pipe to the atmosphere should be open until the pump has attained its normal speed, when it should be turned so as to communicate with the vacuum chambers.

20. One of the two sluice valves on the suction pipes between the pump and the vacuum chambers should be opened while the other is closed.

21. Only one vacuum chamber is in operation at one time, the cock on the moulding press side of the vacuum chamber being left open at the same time as the sluice valve.

22. The water from the moulding presses will be deposited in the vacuum chamber, and when the water level shows on the glass water gauge, the other chamber should be put into operation and the working chamber thrown out of service by changing over the sluice valves, a vacuum cock being provided on each sluice valve to break the vacuum in the chamber, thus permitting the accumulated water to run off into the save-all, through the two-inch cock in the bottom of the vacuum chamber.

23. The cylinder of the vacuum pump should be connected to a small water pipe to permit of water continually running into the cylinder, so as to prevent any particles of nitrocotton which may come over from coming in contact with a dry cylinder wall

24. The vacuum cocks on the moulding presses should be *kept closed* when not in use, so as not to impair the vacuum.

25. The pulp is run into the aluminium hopper from a rubber hose connected to the pulp cock overhead, the hopper being lifted clear after the pulp has settled into the square recesses, and the moulding box rolled into position directly over the moulding press, care being taken to lock the same accurately into position in order to avoid danger of damaging the rams through their not properly entering the moulding box.

26. The valve lever is moved to admit water pressure and the nitrocellulose thereby transferred from the bottom box to the moulding box; the latter being rolled into the finishing press and locked against the distance piece and top cross head by means of the handwheel on top of the press.

27. By operating the valve lever of the finishing press, the nitrocellulose

blocks are pressed, the valve being again moved to relieve the pressure.

28. The handwheel on top of the press is operated to slightly lower the moulding box and the cast iron distance piece is withdrawn.

29. A further operation of the valve lever serves to push the nitrocotton blocks out, ready for packing.

30. Two operators should be at each press; one filling the hopper with pulp, the other operating the finishing press.

Granulation of Nitrocellulose. For special purposes, it is desirable to granulate nitrocellulose without its losing its morphological characteristics or microscopical appearance, as distinguished from gelatinization or colloiding, in the latter of which the structure of the original cellulose has been entirely destroyed. Strictly speaking, granulation is merely mechanical comminution, and therefore in the absence of direct or latent nitrocotton solvents, whereas gelatinization implies the use of direct solvents, either as superficial solvents or as agglutinating media.

In the methods of granulation of Chron[1] and of C. Pieper,[2] the comminution is accompanied by incipient gelatinization, the nitrocellulose being first treated with a small amount of solvent as ethyl acetate, methyl or ethyl alcohols or ether, and as soon as the mass becomes sticky and agglutinates, it is stirred, rolled or rumbled until small distinct granules result.

R. v. Freeden[3] has patented a method for the granulation of nitrocellulose, in which the mixture containing the cellulose ester is treated with a liquid or vapor exercising no chemical or solvent action upon the mass, continuing the agitation until the requisite degree of fineness and porosity is obtained. In the C. Schmidt process,[4] the cellulose is granulated to the desired degree of fineness preliminary to nitration, then treated in the usual manner.

In producing powdered nitrocellulose according to the ideas of H. Wertheim,[1] for the purpose of obtaining a finely disintegrated material especially suitable for impregnation purposes, the pyroxylin in solution is either precipitated by water or by water and steam, or the solution may be mixed with a small amount of water to nearly the point of precipitation, and then steam blown in with violent mechanical agitation. A satisfactory product is formed by dissolving 20 k. of nitrocellulose or celluloid in 40 k. of ethyl alcohol and 5 k. acetone, converted into a solution by means of a kneading machine, after which by the addition of water—in small quantities at first—of a total of 100 k. the precipitation of the nitrocellulose is effected, and may be separated from the solution by subsidence in a very finely pulverulent condition.

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[1] La Nature, 1884, I, 399.

[2] E. P. 2547, 1890. D. R. P. 57399; abst. Mon. Sci. 1892, **40**, 51, 288; Ber. 1892, **25**, 59; Wag. Jahr. 1891, **37**, 428; Zts. ang. Chem. 1891, **4**, 468; Chem. Ztg. 1891, **15**, 1058; 1892, **16**, 1277; Chem. Tech. Rep. 1891, **30**, II, 253; Chem. Ind. 1891, **14**, 375; Industriebl. 1891, 358; Meyer, Jahr. Chem. 1891, **1**, 333; Tech. Chem. Jahr. 1891–2, **14**, 141. In the process for gelatinizing nitrocellulose as described by Elektro-Osmose A.-G. (D. R. P. 309260, 1917; abst. J. S. C. I. 1920, **39**, 430-A), the water is replaced by a gelatinizing liquid by means of electro-osmosis.

[3] U. S. P. 429516, 1890; abst. J. A. C. S. 1890, **12**, 238; Tech. Chem. Jahr. 1890–91, **13**, 152. F. P. 203734; abst. Mon. Sci. 1890, **36**, 874.

[4] E. P. 116, 1904; abst. J. S. C. I. 1904, **23**, 385; Chem. Ztg. Rep. 1905, **29**, 514. See also E. P. 4769, 1895.

A. Voight[2] prefers to first grind the nitrocellulose in an Excelsior mill with the gradual addition of the requisite amount of water, after which the product is placed in a ball mill, whereupon it is ground to a fine amorphous powder in the course of a few hours. This product is then thoroughly washed several times, to remove the less stable portions, the structure thus obtained, according to the patentee, being eminently suitable for the manufacture of compressed nitrocellulose bodies of exceptionally high specific gravity.

There has been granted to F. and P. du Pont a series of patents[3] for the granulation of nitrocotton in which are embodied many of the present-day methods of manipulation. The essence of these patents in their entirety is the suspension of the nitrocellulose in a liquid such as water, which is a strictly non-solvent, and in which is dissolved a suitable salt as calcium chloride, NaCl or sodium nitrate. A solvent of nitrocellulose which is not miscible with the suspending liquid is then added, and the whole then churned up with the addition of steam, thereby granulating the material to any desired degree of fineness. The grains are afterwards solidified by rotation in a drum in an atmosphere of steam. A moderating agent such as nitrated resin or nitrated turpentine is said to be added, and may be dissolved in the solvent used in the granulating process.

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[1] E. P. 6268, 1912; abst. C. A. 1913, **7**, 3025; J. S. C. I. 1913, **32**, 420; Chem. Ztg. Rep. 1913, **37**, 387, 495, 557. Aust. P. Anm. 1755, 1911.

[2] D. R. P. 190073; abst. Mon. Sci. 1910, **71**, 125; Chem. Zentr. 1907, **78**, II, 1881; Chem. Ztg. Rep. 1907, **31**, 614; Wag. Jahr. 1907, **53**, I, 421; Zts. Schiess. Spreng. 1907, **2**, 435.

[3] U. S. P. 503583, 503584, 503585, 503586, 503587, 1893; 519702, 522978, 1894; 590931, 1897; 633611, 1899; abst. J. A. C. S. 1893, **15**, 478; Chem. Ztg. Rep. 1899, **23**, 892. E. P. 15865, 15866, 15867, 1893; abst. J. S. C. I. 1893, **12**, 1057, 1058; Arms and Explos. 1893, **2**, 54. Can. P. 44709, 44780, 44781, 1893. Ital. P. 34706, 1893.

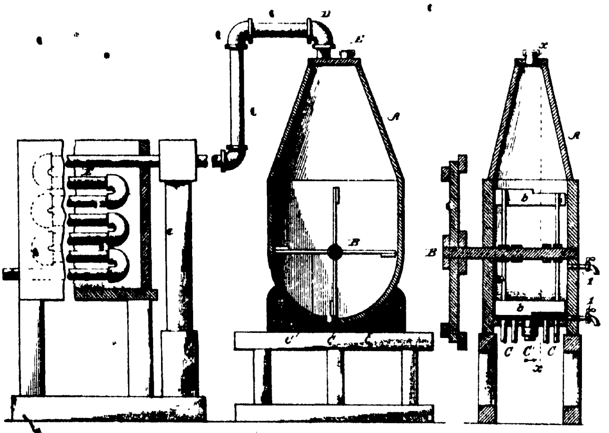

FIG. 281.—DU PONT PROCESS FOR GRANULATING NITROCELLULOSE

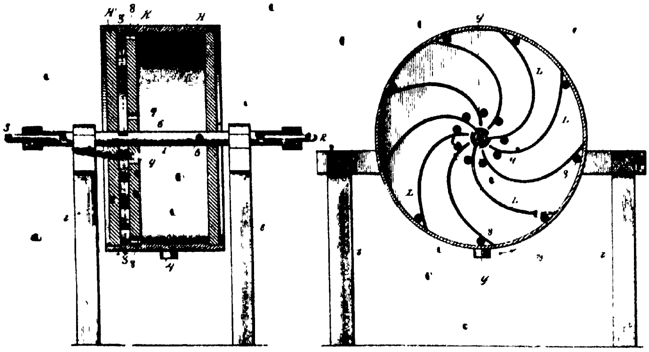

FIG. 282.—DU PONT PROCESS FOR GRANULATING NITROCELLULOSE

A special churn for carrying the process into effect has been evolved and is shown in Figs. 281 and 282, including the apparatus for solidifying the grains. The rotating drum *H* receives the grains, while steam enters by the pipe *2* and opening *5*, and escapes by the passages *9* in the bulkhead *K*. The water leaves the grains by the openings *8*, and is collected and carried off by the revolving chutes *L*, leaving the apparatus with the steam by the openings *6* and pipe *3*.

In a more recent refinement of the above indicated process, E. I. du Pont de Nemours & Co.[1] tumbles a gelatinized nitrocellulose grain with a powdered material which is a solvent for the grain, and then melts the solvent during the continued tumbling operation with a hot aqueous vapor, to impregnate the surface of the grain with the solvent.

For filling a limited space with nitrocellulose, granulated guncotton is often used, as the working of small bodies is often too difficult and time consuming. In one method of producing a granulated product, sheets are formed by means of suitable machinery from the pulp as it comes from the beater, which are then cut in small pieces of the desired size. The pulp still containing water and a small amount of a binder (nitrocellulose solvent miscible with water) is placed in a vessel and agitated until the mass is transformed into granules of the desired size and density. Afterwards the granules may be sorted by sifting.

Colloiding Nitrocellulose. In the general method of presentation of the industrial applications of the cellulose nitrates, Vol. I closes with the fabrication of nitrocellulose to that point where it has been deprived of the contained water by various means, and before the nitrocotton has been treated in any special manner to indicate its use, either in the peaceful or warlike arts. The colloiding of guncotton for smokeless powders is detailed in Vol. VII of this series; colloiding for thermoplastic combinations typified by celluloid is delineated in Vol. V; the colloiding agents, high boilers, thermoplastic bodies, activators, and accelerators form a section of Vol. II under the general heading of fluid and solid solvents and attenuating fluids. Brief reference to these bodies and processes will be found in Chapter XII of this volume.

However, in connection with the topic gelatinization, are a few co-related salient points, which might with propriety, perhaps, be touched upon at this time, and certain processes briefly referred to which are especially interesting in this connection.

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[1] Can. P. 198560, 1920.

The amount of solvent required for the proper colloidation of nitrocellulose varies within comparatively wide limits due to variations in the viscosity and the solubility of the nitrocellulose. For instance, if the viscosity is unduly high, then more solvent is required, and subsequently a longer time is necessary for the removal of the solvent entrained. So that in nitrocellulose intended for smokeless powder and film manufacture, it is advisable to reduce the viscosity for the reasons above stated. The most important colloiding agents at the present time are probably acetone and a mixture of alcohol and ether. Of course, where an excess of the dissolving fluid is used, a true solution results, and upon evaporation of the liquid portion of such a mixture, truly colloided, horny, structureless nitrocellulose remains. If the volume of the solvent be sufficiently reduced, the cellulose ester will merely soften, intumesce and take the form of a plastic paste-like mass, the consistency depending upon the amount of solvent and attenuating non-solvents (if any) employed. Therefore gelatinization or colloidation may be called a transition or intermediate stage between the original cellulose ester and a true solution, the solvency always having proceeded to that stage or phase where the structure of the nitrocellulose has been entirely extinguished. This process of transforming a cellulose ester into a colloid has variously been termed gelatinization, colloidation, colloidization and plastic formation.

It is well known that acetone dissolves the celluloses of maximum nitration, but gives colloids characterized by a deficient tensile strength. Under pressure or shock, their brittleness is so pronounced that they break up, and therefore render such colloids unsuited for smokeless powder, as they are unable to withstand the bursting strain in the gun chamber. The ether-alcohol colloids on the other hand are tough and elastic, although the nitrocelluloses dissolvable in ether-alcohol are of a lower nitration than the guncottons. As ether-alcohols fail to properly gelatinize the celluloses of highest nitration, lower nitrated cottons are used, otherwise ungelatinized fibers will be present which will render the colloid porous, affect its homogeneity and induce excessive pressures and irregular ballistics.

In 1882 W. Reid proposed to harden explosive granulated powders by moistening the grains with a suitable solvent.[1] The next year W. Wolf and F. v. Förster[2] compacted nitrocotton by means of ethyl acetate and nitrobenzene, but it was found that the latter had a too high boiling point, and also was toxic. H. Maxim submitted the guncotton to acetone vapors until incipient gelatinization took place, then removed the excess of solvent and fabricated into the desired shapes.[3] The method of Wolff & Co. was similar.[4] The indurated powder of C. Munroe depended upon the use of nitrobenzene and has been previously mentioned, the nitrocellulose explosive of A. Cronquist being analogous.[5]

In the process of G. Hübner[6] a combination of ether-alcohol and nitronaphthalin was specified, while W. Theodorovic[7] preferred amyl acetate as the gelatinizing medium. A. Luck and C. Cross,[8] and C. Curtis with A. Durnford[9] induced incipient colloidation, then precipitated the mass with agitation aided by small amounts of non-solvents. It has been found that colloided nitrocellulose can be readily granulated by adding to the solution of the cellulose ester small amounts of benzene, toluene or xylene, especially toluene, stirring vigorously until the addition of non-solvent has brought the pyroxylin nearly to the point of precipitation. A large bulk of toluene is then rapidly added with agitation, and the finely granulated nitric ester filtered, washed with gasolene and dried at a low temperature.

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[1] U. S. P. 267108, 1882. W. Reid and D. Johnson, D. R P. 18950; abst. Indbl. 1882, 287; Chem. Tech. Rep. 1882, **21**, II, 175; Wag. Jahr. 1882, **28**, 404; Dingl. Poly. 1882, **246**, 185; Chem. Ind. 1882, **5**, 245, 255; Jahr. Chem. 1882, **35**, 1411; Chem. Tech. Mitth. 1882–3, **32**, 97.

[2] D. R. P. 23808, 1883; abst. Wag. Jahr. 1883, **29**, 389; Chem. Ind. 1883, **6**, 250, 348; Ber. 1883, **16**, 2542; Chem. Tech. Rep. 1883, **22**, II, 188. D. R. P. 26014; abst. Wag. Jahr. 1884, **30**, 377; Chem. Ind. 1884, **7**, 31, 165; Chem. Tech Rep. 1884, **23**, I, 201; Bull. Soc. Chim. 1884, **42**, 398; Poly. Notizbl. 1884, **39**, 187. M. v. Förster, U. S. P. 315357, 1885.

[3] U. S. P. 430212, 1890; 748200, 1903; abst. J. A. C. S. 1890, **12**, 240; 1904, **26-R**, 326; Mon. Sci. 1904, **61**, 99; Chem. Zts. 1904, **3**, 400, 405. E. P. 16213, 1888; abst. J. S. C. I. 1889, **8**, 918. E. P. 16858, 1896; abst. Chem. Ztg. 1898, **20**, 558; Jahr. Chem. 1897, **50**, 1509; Chem. Ind. 1897, **20**, 558; J. S. C. I. 1897, **16**, 698. E. P. 13457, 1903; abst. J. S. C. I. 1903, **22**, 963. F. P. 194792; abst. Mon Sci. 1889, **34**, 756. D. R. P. 49154; abst. Zts. ang. Chem. 1890, **3**, 59; Jahr. Chem. 1890, **43**, 2708; Chem. Tech Rep. 1889, **28**, II, 173; Wag. Jahr. 1889, **35**, 475; Ber. 1890, **23**, 42-R; Industriebl. 1890, 87; Tech. Chem. Jahr. 1889, **12**, 160; Span. P. 8991. Belg. P. 85093. Ital. P. April 16, 1889.

[4] Can. P. 37884, 1891.

[5] Indbl. 1887, 83, 91, 99, 108; abst. Chem. Tech. Rep. 1887, **26**, I, 225.

[6] E. P. 19299, 1894; abst. Arms and Explos. 1895, **3**, 72; J. S. C. I. 1895, **14**, 66. D. R. P. Anm. H, 15323, 1894; abst. Mon. Sci. 1896, **47**, 86. See C. Duttenhofer, E. P. 8776, 1902. Vereinigte Köln-Rottweiler Pulverfabriken, D. R. P. 314317.

[7] E. P. 949, 1896; abst. Chem. Ztg. 1897, **21**, 479; Chem. Tech. Rep. 1897, **36**, I, 198; Mon. Sci. 1898, **52**, 95; J. S. C. I. 1896, **15**, 68, 236, 376.

[8] U. S. P. 665792, 1900; abst. J. A. C. S. 1902, **24**, 51; Mon. Sci. 1901, **57**, 287. E. P. 5286, 18233, 18868, 1898; abst. J. S. C. I. 1899, **18**, 400, 787; Mon. Sci. 1900, **56**, 22, 131; Chem. Tech. Rep. 1899, **38**, 195, 537; 1900, **39**, 325; Chem. Ztg. 1899, **23**, 1077; 1900, **24**, 20; Tech. Chem. Jahr. 1899, **22**, 143. Arms and Explos. 1899, **2**, 66. F. P. 282320; abst. Mon. Sci. 1899, **54**, 187. D. R. P. 117349, 1898; abst. Mon. Sci. 1901, **57**, 148; Chem. Centr. 1901, **72**, I, 288; Chem. Tech. Rep. 1899, **38**, 537; 1901, **40**, 240; Chem. Ztg. 1901, **25**, 93; Jahr. Chem. 1901, **54**, 895; Wag. Jahr. 1901, **47**, 492; Zts. ang. Chem. 1901, **14**, 117. D. R. P. 120562; abst. Mon. Sci. 1901, **57**, 218; 1903,

The Vereinigte Köln-Rottweiler Pulverfabriken[1] produce horny cellulose without dissolving the latter in spirit, this being accomplished by reducing the cotton to a much finer state of subdivision than is usually carried out, and then after partial drying, leaving the material to dry in compressed cakes. W. Borland uses an emulsion consisting of methylated spirit, acetone, camphor and paraffin;[2] while K. Kaiser[3] dissolves acetylene in acetone and uses this mixed solvent as a colloiding agent.

In the preparation of gelatinized cellulose esters according to A. Voswinkel,[4] cellulose is simultaneously treated with zinc chloride, acetic and nitric acids until gelatinization has been effected. This mixed (?) ester is then granulated by means of precipitation by a non-solvent as water, and used as a propellant explosive. The International Smokeless Powder & Dynamite Co.[5] manufacture colloided nitrocellulose of 13.1% N and 95%

59, 283; Chem Tech. Rep 1901, **40,** 238; Chem Ztg 1901, **25,** 425; Tech. Chem. Jahr 1901, **24,** 206; Wag. Jahr. 1901, **47,** 493; Zts. ang. Chem. 1901, **14,** 625. In this connection see also J. S. C. I. 1900, **19,** 642, abst. J C. S. 1900, **78,** i, 541. Mon Sci. 1903, **59,** 114; Chem. Centr. 1900, **71,** II, 698; Chem Tech Rep. 1901, **40,** 574; Jahr. Chem. 1900, **53,** 848; Meyer Jahr. Chem. 1900, **10,** 320; Techn Rundschau d. Berl. Tageblatt. 1901, 38, Berg. Huttenm. Ztg. **60,** 133.

9. E. P. 12591, 1899; abst. J. S C. I 1900, **19,** 689.

[1] E. P. 18930, 1897; abst. Arms and Explos. 1898, **6,** 30; Mon Sci. 1899, **54,** 149; Chem Ztg. 1899, **23,** 10; J. S. C. I. 1898, **17,** 65.

[2] E. P. 4593, 1900; abst. J. S C. I. 1901, **20,** 279; Mon. Sci. 1901, **57,** 287; Chem. Ztg. Rep. 1901, **25,** 619; Chem. Tech. Rep. 1901, **40,** 572.

[3] D. R. P. 144846; abst. Mon. Sci. 1905, **63,** 14; Chem. Centr. 1903, **74,** II, 924; Chem. Ztg. Rep. 1903, **27,** 1011; Chem. Zts. 1904, **3,** 400; Jahr. Chem. 1903, **56,** 1019; Wag. Jahr. 1903, **49,** I, 345; Zts. ang. Chem. 1903, **16,** 1020.

[4] D. R. P. 74070; abst. Zts. ang. Chem. 1894, **7,** 307; Chem. Centr. 1894, **65,** I, 1168; Chem Ztg. 1894, **18,** 612, 1090; Chem. Tech. Rep. 1894, **33,** I, 239; Chem. Ind. 1894, **17,** 512; Wag. Jahr. 1894, **40,** 495; Ber. 1894, **27,** 537-R; Tech. Chem. Jahr. 1893-4, **16,** 165; Meyer Jahr. Chem. 1894, **4,** 418.

[5] E. P. 23252, 1900; abst. J. S. C. I. 1901, **20,** 388. E. P. 13457, 1903; abst. J. S. C. I. 1903, **22,** 963; Chem. Ztg. 1904, **28,** 1030. F. P. 306657;

solubility in ether-alcohol according to a rather complicated arrangement to which the original patent is directed for details of manipulation.

Chlorsulfur compounds,[1] including sulfur di- and tetrachloride, sulfuryl chloride and $SOCl_2$ (thionyl chloride)[2] are specified as being valuable nitrocotton gelatinizers by the patentee, M. Bielefeldt. G. Wadsworth[3] renders nitrocellulose bulky and porous by gelatinizing by means of a suitable solvent in which it is wholly or partially dissolved, then mixing with finely ground barium nitrate and granulating. The barium salt is then removed by treatment with hot water, leaving the porous cellulose ester mass.

J. Bernadou prepares an explosive cementing agent[4] or binder, in which the cementitious material is an ether-alcohol or acetone colloidal nitrocellulose, which during gelatinization has been subjected to a temperature equal to, or below that of freezing water, which produces the colloid in the form of an impalpable powder. W. Williams[5] immerses grains of guncotton in a solution of mononitronaphthalene in a relatively volatile liquid until they begin to soften, when they are removed, dried first by exposure to the atmosphere, and then at a temperature of 40°-70°.

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abst Mon Sci 1902, **58,** 87, Rev Chim Ind 1901, **12,** 146. F. P. 333259; abst. J. S. C I. 1903, **22,** 1308, Mon Sci. 1905, **63,** 84; Chem. Zts. 1904, **3,** 151. D R P 179634, abst C. A 1907, **1,** 2202; Wag Jahr. 1906, **52,** I, 477; Chem Zentr 1907, **78,** I, 1475, Chem Ztg. 1907, **30,** 32; Zts. ang. Chem. 1907, **20,** 1195, Zts Schiess Spreng 1907, **2,** 12

[1] D R P 93351, abst Wag Jahr 1897, **43,** 130, 482; Chem. Centr. 1897, **68,** II, 928, Chem Ztg. Rep. 1897, **21,** 741; Jahr. Chem. 1897, **50,** 1062.

[2] E P 20133, 1900, 20216, 1903; abst. J. S. C. I. 1901, **20,** 1240; 1904, **23,** 836, Chem Ztg Rep 1902, **26,** 254. F. P. 335801, abst J. S. C. I. 1904, **23,** 269, Mon Sci 1905, **63,** 85 D R. P. 95390, abst. Mon Sci 1898, **52,** 178, Chem Centr 1898, **69,** I, 592, Chem. Ztg Rep 1891, **21,** 27; Wag. Jahr. 1897, **43,** 130, 481

[3] U S. P 899577, 1908, abst. C A 1909, **3,** 377; J. S C I 1908, **27,** 1084; Mon Sci 1909, **71,** 128; Zts Schiess Spreng. 1909, **4,** 35. E. P 16492, 1907; abst. C A. 1908, **2,** 2302; J S C I. 1908, **27,** 297; Zts. Schiess Spreng 1908, **3,** 256. The process of T. Reishoff (E P. 10927, 1906) is similar.

[4] U. S P 652455, 652505; E. P. 11567, 1900; 2253, 1901; F. P. 301649, 1900; D. R. P. 125100, 127143, abst J. S. C. I. 1900, **19,** 808, 851; 1901, **20,** 154, 617; Mon. Sci. 1900, **56,** 216, 1901, **57,** 305, 1902, **58,** 145; Rev prod. chim **3,** 341; Chem. Centr. 1901, **72,** II, 1140, Chem. Tech. Rep. 1901, **40,** 570; Chem. Ztg. 1901, **25,** 1019, 1174; Chem. Zts 1902, **1,** 255, 405, Jahr. Chem. 1902, **55,** 1056; Tech. Chem. Jahr. 1901, **24,** 208; Wag. Jahr. 1901, **47,** I, 490; 1902, **48,** I, 366; Zts ang. Chem. 1901, **14,** 1213; 1902, **15,** 19.

[5] U. S. P. 825168, 1906; abst C. A. 1907, **1,** 105, 115; Mon. Sci. 1907, **67,** 52; Chem Ztg. Rep. 1906, **30,** 282; Chem. Zts. 1906, **5,** 495; Zts. Schiess. Spreng. 1906, **1,** 409.

In the gelatinizing apparatus of G. Gentieu,[1] a drum is provided with rotating arms in which the explosive is placed and the gelatinizing liquid forced in by means of a spray nozzle. An automatic pressure valve is provided to keep the supply of liquid constant. J. Delpech[2] obtains colloidal pyroxylin, then filters out the low nitrogen nitrocellulose, thus increasing the stability and insuring more uniform ballistics.

In following the directions of D. Kondratieff,[3] wet nitrocellulose immediately after centrifugalizing and without any other treatment to remove water which it retains, is mixed with alcohol and ether, preferably in the proportions of nitrocellulose 100, alcohol 25, and ether 50 parts, to produce an ordinary gelatinized product. The gelatinization with a sub-class of the urethanes in the hands of W. Rintoul, T. Nolan and Nobel's Explosives Co.[4] in which such bodies as phenylbenzylurethane, benzyl-*o*-tolylurethane are used, have proven a valuable addition in this field, and are mentioned elsewhere in this volume.

Co-nitration. Many attempts have been made, and patents granted for the simultaneous nitration of two or more dissimilar bodies—usually some form of cellulose or a water-soluble carbohydrate in conjunction with glycerol—but in the main, these processes have not been found satisfactory. The object was the formation of explosive combinations upon the theory that a more intimate physical admixture or chemical union might be expected to result, when two dissimilar bodies are nitrated simultaneously.

In the processes as patented by A. Cocking and Kynoch, Ltd.,[5] a nitro body is described similar in properties to nitro-

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1. U. S. P. 832605; abst. Mon. Sci. 1907, **67**, 52; Zts. Schiess. Spreng. 1907, **2**, 57; Chem. Ztg. Rep. 1906, **30**, 412; C. A. 1907, **1**, 489, 498. U. S. P. 837463; abst. Mon. Sci. 1907, **67**, 160; Zts. Schiess. Spreng. 1907, **2**, 135. U. S. P. 856859; abst. Chem. Ztg. Rep. 1907, **31**, 614. G. Gentieu and R. Waddell, U. S. P. 806131, 1905; abst. Mon. Sci. 1906, **65**, 68; Zts. Schiess. Spreng. 1906, **1**, 103; J. A. C. S. 1906, **28**-R, 369.

2. F. P. 436439, 1911; abst. Mon. Sci. 1913, **79**, 186; Chem. Ztg. 1912, **36**, 425.

3. U. S. P. 1212770, 1917; abst. C. A. 1917, **11**, 888; J. S. C. I. 1917, **36**, 403; Mon. Sci. 1917, **84**, 60.

4. E. P. 131389, 1918; abst. J. S. C. I. 1919, **38**, 795-A. In this connection see E. P. 4940, 1913; 14655, 14656, 1915; E. P. Appl. 16616, 1916; 6481, 1917; abst. J. S. C. I. 1914, **33**, 712; 1919, **38**, 340-A, 513-A.

5. E. P. 2836, 1911; abst. Chem. Ztg. Rep. 1912, **36**, 382; Zts. Schiess. Spreng. 1912, **7**, 269, 332; J. S. C. I. 1912, **31**, 303; C. A. 1912, **6**, 1992. E. P. 17221, 1911; abst. J. S. C. I. 1912, **31**, 954; C. A. 1913, **7**, 417. G. Lezinsky (E. P. 22555, 1908; abst. J. S. C. I. 1909, **28**, 817; C. A. 1910, **4**, 113) nitrates together, a resin and a cereal, as wheat. The "glyceropyroxylin" of G.

glycerol, by the nitration of glycerol with sugar dissolved therein. It has been found that sugar may be made to dissolve in glycerol up to about 17% of sugar—although in practice, about 15% may be considered the maximum—and that the product resulting from the nitration of a solution of one in the other is a stable body, and may be utilized for the same purposes and in the same manner as nitroglycerol is employed in the manufacture of explosives.

In carrying the process into effect the sugar is dissolved in the glycerol and nitrated in the usual manner, a liquid nitro body resulting, readily capable of purification because its solubility is of the same order as of nitroglycerol. Cane and beet sugars are preferably employed. On account of its diminished oxygen content, this explosive is inferior in disruptive power to nitroglycerol, from which it cannot be distinguished by appearance. The mixed esters dissolve nitrocellulose, and are alleged to be of peculiar utility in the manufacture of blasting explosives.

The method of J. Blömen[1] relates to the manufacture of high explosives and celluloid compounds, the object being especially to produce an explosive which can be regulated in such a manner as to obtain a greater or lesser degree of force, as may be desired. His process broadly claims the co-nitration of cellulose, a hydrocarbon and a hydroxyl derivative of a hydrocarbon.[2]

These processes of simultaneous nitration—at least in the

Clarke (E. P. 3408, 1868; abst. Mon. Sci. 1870, **12**, 63; Deut. Industrieztg. 1870, 48; Wag. Jahr. 1870, **16**, 217) is formed by impregnating cellulose with glycerol, which is then nitrated.

[1] E. P. 9984, 1901; abst. J. S. C. I. 1901, **20**, 1140; Chem. Ztg. 1902, **26**, 902. U. S. P. 599589, 674159, 674291; abst. J. A. C. S. 1902, **24**, 106; Mon. Sci. 1901, **57**, 287. Can. P. 74321, 74322, 1901.

[2] See also H. Maxim, E. P. 5209, 1890; abst. J. S. C. I. 1890, **9**, 438; 1891, **10**, 292, 484. The Satanite Powder Co. have described (E. P. 7719, 1911; abst. J. S. C. I. 1911, **30**, 1186; C. A. 1912, **6**, 2848; Chem. Ztg. Rep. 1912, **36**, 531) the co-nitration of resin and starch.

In connection with the subject of co-nitration of cellulose and glycerol, and the nature of the products formed by combination of the two esters, the work of D. Chiaraviglo and O. Corbino (Atti. accad. Lincei, 1915, **24**, I, 247; abst. J. S. C. I. 1915, **34**, 637; C. A. 1915, **9**, 2148; Chem. Zentr. 1917, **88**, I, 1029; Annali Chim. Appl. 1915, **3**, 27C) is illuminating. The gelatinization of guncotton, which is so important in the manufacture of explosives, is usually accomplished by means of a volatile solvent, or by some other substance which is usually explosive but little volatile and which is retained in the final product as an essential constituent. Mixtures of nitroglycerol and nitrocellulose are considered to be colloidal but their structures, and degree of homogeneity are not known (cf. E. Paterno and F. Traetta-Mosca, Gazz. chim. ital; Zts. Schiess. Spreng. 1909, **5**, 144). They (C. and C.) placed a layer of powdery nitrated cotton in the bottom of a large flask, in the center of which a beaker containing nitroglycerol was placed, the flask being at-major number of instances—have proven of but little commercial value, some of the disadvantages which seem to be inherent being:

1. The nitrating mixture found most desirable for one of the bodies has been found unsuitable for the esterification of the other.

2. The temperature, length of immersion, composition of the nitrating bath and other details for the most favorable nitration of one of the bodies, is wholly inapplicable to the other where maximum yield of acceptable purity and stability is aimed at.

3. The yields are inferior as compared with the nitration of each separately in a bath best suited to produce the maximum yield and desirable properties.

4. Often it is unusually difficult to wash to neutrality bodies of dissimilar chemical structure and physical appearance, without materially diminishing the yield.

Therefore at the present day, cellulose bodies together with glycerol, sugars and petroleum hydrocarbons, are seldom, if ever, simultaneously nitrated in the same bath. With glycerol and the water-soluble carbohydrates, more satisfactory results are obtainable.

Classes of Cellulose Nitrates Produced in the United States. For practical purposes, these may be reduced to three general classes, with a number of specialized subdivisions as follows:

(1) Pyrocollodion, entirely soluble in acetone, and 95% or

tached to a special form of apparatus (described in Atti accad. Lincei, **23** I, 37). The whole was evacuated with a mercury vacuum pump and kep in a large air thermostat at a constant temperature of 30°. The glycery nitrate was gradually evaporated from the beaker at a rate which diminished until after some days it was imperceptible At the end of the experimen the guncotton was found apparently to have sustained little change except that it was a little more sticky. But at high pressures, transformatio into a homogeneous, transparent, gelatinous mass took place. When th experiment was conducted at 30°, a collodion cotton (12.25% N) took u 31.5% nitroglycerol in 7 days, and 35 6% in 40 days. A guncotton (13.27 N) took up 37.4% in 40 days. From the fact that when glyceryl and cellu lose nitrates are brought together a marked rise in temperature was observe leads to the inference that the process is not simply the solution of a solid in liquid, but a true exothermic chemical reaction between the two classes esters, or else the facts must be ascribed to simple imbibition phenomena.

In the method of the co-nitration of cellulose and sugar of C. Dittma (E. P. 3088, 1875; abst Wag. Jahr. 1877, **23**, 384; Ber 1877, **10**, 725; Chem Tech. Rep. 1877, **16**, I, 487) the cellulose in the form of pulp is soaked in solution of sugar or mannite, then dried, and nitrated in the usual manne thus producing a nitrated cellulose with nitrosaccharose or nitromannite.

better in ether-alcohol, used as the official Government explosive for military uses, manufactured either by centrifugal nitration (Naval Station, at Indian Head, or various du Pont works) or by the displacement method (Picatinny Arsenal, Dover, N. J.). Under this heading is also to be included various sporting powders for rifle and shotgun use, although the nitrogen content in these usually falls below pyrocollodion powders. Comparatively speaking, but little cellulose is commercially nitrated over 13% N.

(2) Nitrocellulose for pyroxylin solutions, of high grade linters stock, nitrogen percentage around 12, solubility high, and free flowing in viscosity. Used in pyroxylin lacquers, and to a less extent for banana liquids and bronzing mixtures. The nitration of tissue paper for "water white" lacquers for the protection of silverware, with a nitrogen percentage of 11.5–12, is an important branch of this subdivision. The manufacture of continuous photographic films which are cast (deposited) from an acetone solution, are examples of low viscous esters, while the highly viscous celluloids are prepared from tissue paper, but of a much lower nitrogen content. In the production of nitrocellulose for colloiding with nitroglycerol in blasting gelatin manufacture, it is essential that the solubility shall be unusually high, and a great improvement in this direction has been made by the discovery of the technical staff of Nobel's Explosives Co., Ltd., of a series of accelerating solvents or "activators" mentioned elsewhere herein.

(3) Nitration of tissue paper for plastic formation, high viscosity coupled with a satisfactory solubility, nitrogen content about 10.7%, and producing with camphor and analogous bodies products of high thermoplasticity and tensile strength. Irrespective as to whether tissue paper is used as the initial material (celluloid formation), or hull fiber or shavings (artificial leather coating compositions), the manufacturing cost is low, the yield comparatively high, and the solubility not always satisfactory.

Actual factory details for the manufacture of each of these three classes of nitrated celluloses, are described in detail subsequently.[1]

From a factory cost viewpoint, the amount of nitrating acid retained in the manufacture of the above classes is highly important. In general, it is found that the physical condition of the original cotton fiber has considerable influence upon the amount of acid retained upon wringing, in that an open or "pilled" fiber causes less acid to be retained than does a matted fiber, due primarily to the fact that the latter upon nitration packs closely in the wringer, and prevents or rather retards the removal of the acid. This, of course, is materially influenced by the speed of revolution of the centrifugal, the charge contained therein, the size of the perforations in the centrifugal basket, and the period in which the nitrated cotton is centrifugalized. Where notable variations in the peripheral speed of the wringer takes place, corresponding variations are found in the amount of acid retained.

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[1] A process for the preparation of "soluble cellulose" has been described by P. Marino (E. P. 7430, 1908; abst. J. S. C. I. 1909, **28**, 812) in which ordinary pyroxylin is introduced into a mixture of alcoholic solutions

Specifications for Guncotton for the United States Navy.

1. *Raw Materials.* (a) *Cellulose.* The material to be used is bleached cellulose, prepared for nitrating, which will be obtained by purifying unspun cotton waste, or suitable short fibered commercial cotton, and thoroughly washing to remove the purifying material or salts; it is to contain not more than 0.4% of extractive matter and not more than 0.8% of ash; it is to be of uniform character, clean, and free from such lumps as will prevent uniform nitration. It should not contain more than "traces of lime, chlorides or sulfates."

The extractive matter will be determined by extracting not less than 1.5 gm. of cotton in a Wiley or Soxhlet extractor with ethyl ether and weighing the extracted matter after drying at 100° C.; the percentage is to be calculated on dry cotton. Ash will be determined by digesting about 1.5 gm. of cotton with a

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containing about 10% (of the weight of the pyroxylin) of each of the following substances: manganese chloride, ferric sulfate, and sodium ethyl sulfate. The solution is diluted with ether or other solvent of pyroxylin and the pyroxylin is dissolved. A saturated solution of freshly precipitated ammonium magnesium phosphate is separately prepared in a quantity of sulfuric, phosphoric, or other mineral acid equivalent to about 10% of that of the solvent used with the pyroxylin. The two solutions are mixed and heated at 25° for twelve hours. The "soluble cellulose," which separates on cooling, is drained, washed and dried. The mother liquors are collected separately, and after dilution with spirit and neutralization of the mineral acid, they may be utilized for rendering wood or fabrics non-inflammable. J. Blomen, J. A. C. S. 1895, **17**, 411; abst. Bull. Soc. Chim. 1895, **14**, 957; Chem. Centr. 1895, **66**, I, 1090; Jahr. Chem. 1895, **48**, 1359. For the alcohol-soluble nitrocellulose called "alkolen," see Poly. Centr. 1863, **29**, 700.

little pure nitric acid, incinerating at a red heat and weighing the residue; the percentage to be calculated on dry cotton.

Moisture will be determined by drying not less than 3 gm. of cotton at 105° C., to constant weight.

(b) *Acids.* A mixture of sulfuric and nitric acids will be used, containing no metallic salts other than salts of iron, and not more than a trace of chlorine compounds.

(c) *Ether.* Ethyl ether will be used, containing no impurities other than small quantities of water and ethyl alcohol. The ether to be clear and colorless, with characteristic pure odor, having less than 0.006% acidity, calculated as acetic acid, and less than 0.002% residue after evaporation and drying at 100° C.; and specific gravity at 20°/20° C., to be from 0.717 to 0.723.

(d) *Alcohol.* Ethyl alcohol, 92.3% absolute (by weight) will be used; it is to be of the best quality, clear and colorless with characteristic pure odor, having less than 0.006% residue after evaporation and drying at 100° C., and acidity less than 0.01%, calculated as acetic acid. It shall be subjected to the silver nitrate test, as follows:

$$\left.\begin{array}{l}3\text{ gm. AgNO}_3\text{, c p.}\\ 3\text{ gm. NaOH, c p}\\ 20\text{ gm. NH}_4\text{OH, c. p.}\end{array}\right\}\text{ Make up to 100 cc.}$$

Ten cc. of the sample, diluted with 10 cc. of water, to be placed in a tight bottle and 1 cc. of the silver nitrate solution added. Allow to stand one hour in the dark and examine for unreduced silver salts in clear solution, after filtering; if such are found, the alcohol contains less than the allowable amount of aldehyde.

The strength of alcohol is calculated by the use of the alcohol tables given in the latest edition of Allen's "Commercial Organic Analysis."

(e) Ether and alcohol obtained from any of the manufacturing processes as recovered solvent are, before use for colloiding, to be put in condition for fulfilling the requirements of (c) and (d).

(f) *Graphite.* If graphite is used on the surface of powder grains, or is incorporated in the powder, it shall be dry, ground very fine, and shall not contain more than a trace of silicates or compounds of sulfur, and shall be free from sulfur and acids.

(g) *Carbonate of Soda.* The best quality of refined alkali, free from sulfides, containing not less than 96% of Na_2CO_3, calculated on dry samples, will be used.

2. *Nitrocellulose—Manufacturing Processes.* (a) *Quality.* (1) The nitrocellulose in finished poacher lots shall have a nitration of 12.60%, ±0.1%. These lots may be made up by blending nitrocellulose which contains from 12.45% to 12.75% nitrogen and at least 95% solubility.

(2) It shall have a solubility of at least 95% at 15.5° C. in a mixture of two volumes of ether and one volume of alcohol both of the standard quality prescribed by these specifications.

(3) It shall contain less than 0.4% of material insoluble in acetone.

(4) It shall leave after ignition, less than 0.4% of ash.

(5) It shall give a heat test of 65.5° C. with potassium starch paper, of at least thirty-five minutes.

(6) It shall give a German test at 135° C., with litmus paper of at least 30 minutes.

(7) It shall contain no alkali, mercuric chloride, or other substances which will mask the heat test in any way.

(8) It shall be uniformly pulped, free from lumps, strings or material of such consistency as to effect proper colloiding in the mixers.

(b) *Nitrating.* Cellulose of standard quality shall be thoroughly dried at a temperature not exceeding 110° C. When cold, this cellulose shall be nitrated in mixed nitric and sulfuric acids. After nitrating the nitrocellulose shall be washed with water before boiling.

(c) *Preliminary Boiling.* The nitrocellulose shall next be boiled for at least 40 hours, with not less than four changes of water, in tubs so constructed that the nitrocellulose shall not come into direct contact with the heating coils (or with the steam from the coils). There shall be complete ebullition, or boiling, over the entire surface of the tubs. No alkali shall be used in the preliminary boiling.

(d) *Pulping.* The nitrocellulose shall next be pulped in fresh water, to which is added just enough sodium carbonate solution to preserve a slight alkaline reaction to phenolphthalein solution, the process to continue until the material is thoroughly and evenly pulped to a satisfactory degree of fineness and shows a clean break when a handful is squeezed and broken into parts. During the process the water shall be changed to such an extent as may be necessary to remove impurities.

(e) *Poaching.* After pulping, the nitrocellulose pulp shall be run into the poachers, settled, and the water decanted. The nitrocellulose shall then be boiled for 6 hours in fresh water, during which time a total of not more than 10 gallons of carbonate of soda solution for each 2000 pounds of dry nitrocellulose may be added at intervals; this solution shall contain 1 pound of carbonate of soda to the gallon. During this and all other boiling in the poachers the pulp shall be thoroughly agitated by mechanical stirrers. After boiling, the nitrocellulose shall be allowed to settle and the clear water decanted as completely as possible. The tubs shall then be filled with fresh water, boiled for 2 hours, settled, decanted and refilled with fresh water. The boiling shall then be continued for 1 hour, and this process repeated three times, making a total boiling treatment in the poachers as follows:

Six hours' boiling, with or without sodium carbonate, settle, change water.

Two hours' boiling, no soda, settle, change water.

One hour boiling, no soda, settle, change water.

One hour boiling, no soda, settle, change water.

One hour boiling, no soda, settle, change water.

One hour boiling, no soda, settle, change water.

Total, twelve hours' boiling with six changes of water.

After boiling, the nitrocellulose shall have ten cold-water washings, each washing to consist of agitation, by mechanical means, for one-half hour, in sufficient amount of fresh water, thorough settling and decanting the clear water; in decanting at least 40% of the total contents of the poacher shall be drawn off. A sample shall then be taken for subjection to the various tests prescribed for nitrocellulose. Should the nitrocellulose fail to meet the required heat tests, it must be boiled again with two changes of water, the time of actual boiling being five hours, without the use of alkali, and must then be given the ten cold water washings in the manner prescribed for the regular treatment.

The utmost cleanliness shall be observed in manufacture. All machinery, tools, and appliances shall be kept in the condition necessary to prevent the incorporation in the nitrocellulose of foreign matter of any kind. At all stages of the process the water used shall be clean and free from deleterious matter.

3. *Testing Nitrocellulose.* (a) *Sampling.* Each poacher lot or blend will be given a designating number. A sample, of about 150 gm. dry weight, shall be selected by the inspector from each poacher charge after purification is complete, and this shall be properly marked and sent for examination. If a lot or blend is made up by blending various weights of nitrocellulose of nitration of 12.45% to 12.75% each nitrocellulose included therein shall be similarly sampled for analysis.

(b) *65.5° C. Heat Test with Potassium Iodide Starch Paper.* The sample shall be pressed in a clean cloth or wrung in a wringer, if it contains a large excess of water. The cake shall be rubbed up in a cloth until fine, taking care that it does not come in contact with the hands, spread out on clean paper trays, and dried in an air bath at 35° to 43° C. for a sufficient length of time to reduce the moisture to the amount required to give a minimum heat test, this amount being from 1.5% to 2%. If, as sometimes happens in dry weather, the moisture has been reduced to less than 1.5% the sample shall be placed in a moist atmosphere for a time not exceeding two hours, until the required moisture percentage is obtained. The whole time of drying and making the test shall not exceed eight hours.

The dried sample for the heat shall be weighed out in five test tubes 1.3 gm. (20 grains) to each tube, so that a series is obtained covering the widest variation allowed for moisture. These tubes are standard, $5^{1}/_{2}$ inches long, $^{1}/_{2}$ inch internal diameter, and $^{5}/_{8}$ inch external diameter, closed by a clean cork stopper, fitting tightly, through which passes a tight glass rod with platinum holder for the paper; corks are discarded after one test. The nitrocellulose is pressed or shaken down in the tube until it occupies a space of $1^{5}/_{8}$ inches. The test papers, about 1 inch in length and $^{3}/_{8}$ incn wide, are hung on the platinum holders and moistened on the upper half with a 50% solution of pure glycerol in water. The heating bath, carefully regulated at 65.5° C ± 1° C., is placed so that a bright, reflected light is obtained, and tubes placed in the bath. As test continues a slight film of moisture condenses on inside of tubes, and line of demarkation between wet and dry test paper is kept abreast the lower edge of the moisture film. The first appearance of discoloration of the damp portion of the test paper marks the end of the test from each separate tube, the minimum test of any one of the five tubes being the heat test of the nitrocellulose. The discoloration is to be greater than that obtained at the same time by a blank test. Standard test papers will be used and will be furnished by the department to manufacturers. The standard water bath holds ten tubes and is made long and narrow, to reduce to a minimum the heating of the upper portion of the tubes. These tubes are immersed in the bath to a standard depth of 2.25 inches.

(c) *"German" Test at 135° C.* A sample of nitrocellulose shall be dried at ordinary laboratory temperature over night, and for the heat test; 2.5 gm. of the material are to be pressed into the lower 2 inches in each of the two tubes, of heavy glass about 290 mm. long, 18 mm. outside diameter and 15 mm. inside diameter, closed with a cork stopper through which a hole 4 mm. in diameter has been bored. A piece of standard blue litmus paper 70 mm. long and 20 mm. wide is placed in each tube, its lower edge 25 mm. above the cotton. When the constant temperature bath has been carefully regulated at 134.5° C. ± 0.5° C. these tubes are placed in the bath so that not more than 6 or 7 mm. of the length projects from the bath. Examination of the tube is made by withdrawing about one-half its length and replacing quickly, each five minutes, after twenty minutes have elapsed.

The bath must be placed in a good light and with a suitable background. The standard litmus papers will be furnished by the department. The test shall be considered completed when the litmus paper is entirely reddened, and the minimum test of either tube shall be taken as the test of the lot. The standard red color must not be obtained in less than thirty minutes.

(d) *Nitration.* The nitration will be determined on a 1-gram sample of nitrocellulose after drying for an hour and a half at 95° to 100° C. or in a vacuum dryer after a thorough air drying. The nitrocellulose is to be washed into a du Pont nitrometer by 20 cc. of H_2SO_4 and the per cent. of nitrogen determined by comparison of the gas given off with a standard volume. The acid used shall be c. p. sulfuric acid containing 94% to 96% H_2SO_4.

The nitrometer is standardized by preparation of a calculated volume of dry air at a temperature of 20° C. and 760 mm. pressure at 20° C. in the comparison tube. When pure potassium nitrate is tested with the standard sulfuric acid against such comparison tube, the nitrogen figure should invariably be 13.85%.

(e) *Ash and Organic Residue.* Ash will be determined by decomposing the nitrocellulose with nitric acid, igniting and weighing the residue. The per cent. of organic residue will be obtained by dissolving 1 gm. of nitrocellulose in pure acetone, filtering by decantation, and finally, on an asbestos filter, drying and then determining the loss by ignition.

(f) *Insoluble Nitrocellulose.* The amount of insoluble nitrocellulose will be determined by soaking 1 gm. of the dry sample overnight in 95% alcohol. On the following morning the mixture will be brought to 15.5° C. and a sufficient amount of ethyl ether, at the same temperature, added to make the mixture of ether-alcohol 2 to 1, by volume; the mixture is to be kept at 15.5° C. for one hour. The insoluble nitrocellulose is then to be filtered off and weighed, a correction for the ash and organic material insoluble in acetone being made.

When the amounts of insoluble nitrocellulose and organic residue are very small, comparative volumetric readings may be made in long tubes, allowing the insoluble material to settle after regular treatment for solution in the solvents. The lower portions of these tubes are constricted to one-half inch in diameter, cylindrical shape, and graduated by direct weighing of residue.

(g) *Solubility.* The amount of soluble nitrocellulose will be found by subtracting the sum of the ash, organic residue, and insoluble nitrocellulose from 100%.

(h) *Acceptance.* Lots of nitrocellulose, which after chemical examination have been found satisfactory, shall be provisionally accepted, subject to the powder made therefrom successfully passing the specified ballistic and chemical tests.

United States Specifications for Nitrocellulose or Pyroxylin.

The specifications for cotton before colloiding are, nitrogen 12.6 + or —0.2; solubility 95% in one part alcohol to two parts ether by volume; heat test 30 minutes at 65.5° C.; test with litmus for 30 minutes at 135° C.

Specifications for nitrocellulose powder:

Volatiles 3.8%, normal dryhouse conditions; 0.4% diphenylamine; test with litmus for one hour at 135° C. Powder should not explode within four hours at 135° C.

In the powder some variation from true plane must be allowed for warping or curling (say, one second on the width ordinate of curve).

British Specifications for Guncotton. 1. The guncotton should, in every respect, be equal to the guncotton manufactured at the Royal Gun Powder Factory, Waltham Abbey.

2. If the displacement process is in use, a period of at least $2^1/_2$ hours for nitration is required. The guncotton should be boiled according to the following scheme.

12 hours plus 12 hours plus 4 hrs. plus 4 hrs. plus 4 hrs. plus 4 hrs. plus 2 hrs. A convenient proportion is 1 gal. to 1 lb. cotton. After boiling, the wash water is displaced upwards by cold water for the next boiling.

The guncotton must be boiled in the unpulped condition, as it comes from cold water washing after nitration. It is essential that the first boiling of 12 hrs. should be conducted in an acid solution approaching in strength 1% on the guncotton. This acid is normally disengaged from the guncotton. The next boiling may be slightly acid, but the final boilings must be in water with an alkalinity of about 27 parts as ($CaCO_3$) per 100,000. If the natural alkalinity of the water be less than this, it should have Na_2CO_3 added to it, to bring it up to the equivalent of 27 pts. $CaCO_3$ per 100,000. Should the water be a hard one, it may be found that the required residual $CaCO_3$ has been deposited on the fiber. If this is not the case, the deficit from the quantity required by this specification may be added by working in chalk in the poacher, or by adding to the water in the poacher a small quantity of calcium hydrate solution and precipitating $CaCO_3$ from this on to the fiber by means of Na_2CO_3 solution. Soluble alkali should be washed out by water.

3. The guncotton must be free from grit and should not contain any mineral other than that naturally present in cotton, or taken up from the wash water, and such as may unavoidably have been taken up from the machinery employed in the manufacture.

The total quantity of mineral matter contained in the guncotton must not exceed one per cent by weight.

This is determined by mixing a suitable restrainer such as a strong solution of ammonium sulfite, igniting off all organic matter and sulfating the ash.

4. The guncotton must be free from unconverted cotton, and from all matter not permitted by the specification.

5. *Alkalinity.* The guncotton must contain from 0.2% to 0.4% of $CaCO_3$, calculated on the dry material and estimated by the following process.

Shake 10 gm. of guncotton for 1 hr. with 100 cc. N/10 HCl and 100 cc. distilled water in a tall glass cylinder; settle for 1 hr., remove 100 cc. of the clear liquid by a pipette, and titrate with N/10 Na_2CO_3 using methyl orange as an indicator.

The alkalinity of the sample is calculated as % of $CaCO_3$ on the dry guncotton from the volume of standard acid neutralized by the guncotton.

6. *Nitrogen.* The % of N is to be calculated on the guncotton free from mineral matter, and is not to be less than 12.9% nor more than 13.2%, the estimation being carried out as follows:

About 0.5 to 0.52 gram of perfectly dry guncotton, very finely divided, is weighed in a stoppered weighing bottle; 5 cc. of pure 96% sulfuric acid are added and stirred with the guncotton until the mixture can be poured into the cup of a 150 cc. nitrometer. The residue in the weighing bottle and nitrometer cup is washed into the nitrometer with a further 9.5 cc. of acid in several portions, 0.5 of distilled water being added to the last portion of the acid. The nitrometer is then shaken and when the reaction is completed and the temperature has become steady the volume of nitric oxide gas is measured and reduced to 0° and 760 mm. pressure. From the volume the % N in sample is calculated.

The guncotton for the nitrometer test must be taken from the poacher before alkaline matter is added.

7. *Soluble in Ether-Alcohol.* The % of nitrocotton soluble in ether-alcohol is not to exceed 12% on the dry guncotton. The estimate is carried out as detailed in Chapter XI.

8. *Organic Matter Insoluble in Acetone.* The % of organic matter insoluble in acetone is not to exceed 1% on the dry guncotton. The total insoluble in acetone is determined, and the

loss on ignition after converting the ash into carbonates is reported as organic matter insoluble in acetone.

9. *Sulfate.* The total sulfate present, calculated as sulfuric acid on dry cotton, must not be more than 0.1% when estimated by the following process.

5 gm. of guncotton are dissolved in 50 cc. of nitric acid, sp. gr. 1.5. When solution is complete a few crystals of $KClO_3$ are added to the solution, which is evaporated nearly to dryness over an argand burner; 5 cc. HCl are added followed by 0.5 gm. of $KClO_3$ in successive small portions and the mixture evaporated almost to dryness. The treatment with HCl and potassium chlorate and the evaporation are repeated, the residue is dissolved in water, filtered and sulfuric acid estimated in the filtrate which should measure 150 cc.; the $BaSO_4$ ppt. is allowed to settle over night. A blank estimation of sulfate is made on all reagents and the result subtracted.

10. *Heat Test.* As laid down in Cordite specification P161C.

11. Will test.

The guncotton when subjected to the Will test (for details see Robertson, J. S. C. I. 1903, 819) should disengage from 2.5 gm. not more than 6.5 mg. of N in 4 hrs.

French Guncotton and Smokeless Powder Requirements.

1. *Raw Materials. Cellulose,* shall contain not more than 0.4% of extractive matter and not more than 0.8% of ash. It is to be uniform and clean, and contain not more than traces of lime, chlorides or sulfates.

2. *Acids.* A mixture of sulfuric and nitric acids containing no metallic salts other than salts of iron, and not more than traces of chlorine compounds shall be used.

3. *Ether.* Ethyl ether will be used, containing no impurities other than small quantities of water and ethyl alcohol the ether to be clear and colorless, with characteristic pure odor having less than 0.006% acidity, calculated as acetic acid, and less than 0.002% residue after evaporation and drying at 100° C. the sp. gr. at 20° C. to be from 0.717 to 0.723.

4. *Alcohol.* Ethyl alcohol will be used containing not less than 92.3% ethyl alcohol by weight, to which shall have been added 0.5% benzol. The mixture shall give not more than 0.006%

residue at 100° C. acidity not more than 0.01% calculated as acid.

5. *Ether or Alcohol.* Before use for colloiding to be put in condition for fulfilling the requirements of (3) and (4).

6. *Graphite.* If used shall be dry, ground very fine, and shall contain not more than trace of silicates or compounds of sulfur and shall be free from sulfur and acids.

7. *Carbonate of Soda.* The best quality of refined alkali, free from sulfides containing not less than 96% of Na_2CO_3 calculated on dry samples will be used.

1. *Nitration of Cellulose.* Nitrocellulose shall contain not less than 12.5% nitrogen, and shall have a solubility of at least 80% at 15.5° C. in a mixture of two volumes of ether and one volume of alcohol, both of the standard quality prescribed by the specifications.

2. It shall contain not more than 0.4% material insoluble in acetone.

3. It shall have after ignition less than 0.4% ash.

4. It shall give a heat test of 65° C. with potassium iodide starch paper, of at least 35 minutes.

5. It shall give a stability test at 135° C. with normal methyl violet paper, of at least 25 minutes.

6. It shall contain no alkali, mercuric chloride, or other substance which will mask the heat test in any way.

7. It shall be uniformly pulped, free from lumps, strings or materials, of such consistency as to effect proper colloiding in the mixers.

British Admiralty Specifications A-121 for Guncotton Slabs for Mines. 1. The cotton waste used in the manufacture of the guncotton is to comply with the specification in Appendix I.

2. The guncotton of which the primers and slabs are made is to comply with the following conditions, which will be determined as laid down in the several tests in Appendix V:

(a) *Nitrogen.* The percentage of nitrogen is to be calculated on the guncotton free from mineral matter and is not to be less than 12.9% nor more than 13.2%.

(b) *Soluble in Ether-Alcohol.* The percentage of nitrocotton soluble in ether-alcohol is not to exceed 12% on the dry guncotton.

(c) *Organic Matter Insoluble in Acetone.* The percentage of organic matter insoluble in acetone is not to exceed 1% on the dry guncotton.

(d) *Alkalinity.* The total alkalinity calculated as percentage of calcium carbonate is not to be less than 0.8%, nor greater than 1.5% on the dry guncotton.

(e) *Mineral Matter.* The guncotton is to be free from grit and is not to contain any substance other than that naturally present in cotton, or unavoidably taken up from the water and the machinery employed in the manufacture.

The total mineral matter present is not to exceed 2% on the dry guncotton.

The most suitable method of adding alkaline matter will probably be found to be as follows:

After the pulp has been washed, sterilized, and purified in the usual way, the wash water is to be removed, and so much of a clear saturated solution of lime water is to be added as will give, as a final alkaline content, the prescribed amount. The pulp is to be thoroughly stirred up in this lime water, and a solution of carbonate of soda, sufficient to precipitate the whole of the lime, is to be added: the pulp is then to be again well stirred up.

After this stirring, the soda salts are to be removed by at least three washings.

If any departure from this method is desired, a detailed description of the procedure it is proposed to adopt must be furnished to, and the written sanction of the Army Council obtained.

(f) *Heat Test.* The guncotton, either in the form of pulp, or when compressed into primers or slabs, is to stand a heat test as laid down in Appendix V (4) of not less than 10 minutes at 170° F. (76.7° C.).

3. The guncotton shall, in every respect, be equal to the guncotton manufactured at the Royal Gunpowder Factory, Waltham Abbey. A sample from each poaching of guncotton will be selected by an officer of the Royal Gunpowder Factory, Waltham Abbey, for the purpose of carrying out the tests laid down in paragraph 2, and a test number allotted to the poaching. The contractor will be informed of the result of the test, and any poaching not giving satisfactory results will be rejected.

4. The guncotton will be issued in the form of "pulp" con-

taining a maximum of thirty five to forty per cent of water.

Unless specified herein that the packing cases shall become the property of the War Office, they will remain the property of the contractor, who will be responsible for their removal. Should they not be removed within two months of the acceptance of the stores, they will be disposed of, and in such circumstances the contractor will not be entitled to make any claim for compensation.

The packing cases must be marked "Returnable" or "Non-returnable."

5. The Superintendent Royal Gunpowder and Small Arms Factories will, on application, afford the contractor any information in his power which may facilitate the completion of the contract.

6. The guncotton may be inspected during manufacture by, and after delivery will be subject to testing by, and to the final approval of, the Superintendent Royal Gunpowder and Small Arms Factories, or an officer deputed by him, who will be at liberty to take samples of any of the materials used, or of the guncotton itself, at any stage of its manufacture.

7. The contractor will be required to supply, free of charge, sufficient guncotton for the purpose of examination and testing.

The British Army Ordnance Service Regulations of War Office Regulations, 1914, Part 2, page 89, gives the following for the examination of dry guncotton and tonite:

425. Every six months (about the 31st March and 30th September) at tropical stations, and every year at non-tropical stations, one cylinder from each of half the number of packages of *all* dry guncotton and 10% of tonite charges from each package in every store, will be inspected and tested for free acid, and reports made on A. F. G. 931.

426. At each subsequent inspection, the proportion of guncotton to be inspected is to be taken from packages and cylinders not previously opened, so long as such exist, and afterwards in the order of date of the previous inspections.

427. The inspections should be conducted in a locality where the atmosphere is not damp.

428. To test the guncotton, remove it from the package and apply a piece of blue litmus paper, which has been moistened with clean water, to the face of one of the primers, a small portion of the

surface, if coated with paraffin wax or gelatinized with acetone, being removed, and then press another primer upon it. If guncotton yarn is being tested, the moistened test paper should be laid in a fold of the yarn which must be turned back and held down against the paper by the forceps.

429. If the litmus paper remains blue, or if it is not decidedly reddened, remove it, rub away any moisture, and dry the guncotton with a piece of clean cotton waste or by repeatedly pressing some clean blotting paper upon it; replace the guncotton, if it has been removed, and close up the cylinder.

430. If the paper becomes red, the guncotton should be destroyed by burning as laid down in paragraph 446. If this cannot be done at once, the whole contents of the cylinder should be immersed in water and destroyed as soon afterwards as possible.

431. Should any guncotton redden the test paper, the whole of the cylinders in its package, and also a further proportion of 10% of the cylinders similar to that in which it was found, will be inspected. If by this inspection any further defective guncotton is found, the whole of the cylinders in store are to be inspected and action taken as in paragraph 430.

Prussian Regulations Regarding Moist Nitrocellulose.[1]

Moist nitrocellulose, also including moist collodion cotton, is considered to be an explosive and is subject as such to the Police Orders Concerning the Trade in Explosives of September 14, 1905, and the Schedule C of Railroad Transportation of December 23, 1908. As moist nitrocellulose has not been included in the ordinance adopted by the Bundesrath on April 29, 1908, and which concerned mainly explosives, wet nitrocellulose shall be disposed of only to persons holding a police permit for the possession of explosives. The amount of such explosives has no bearing on the subject.

[1] Ministerial Publication, Commerce and Trade, Nov. 21, 1910.

CHAPTER XI.

ANALYTICAL DETERMINATIONS OF THE CELLULOSE NITRATES.

The tests detailed in this chapter are primarily those as applied to nitrocellulose in the non-colloid state as distinguished from the colloided cellulose nitrate smokeless powders and explosives. For this reason the ballistic and other similar tests are omitted herein, being reserved for consideration with the volume (VII) dealing specifically with nitrocellulose-containing explosives. Similarly, those tests of especial moment in connection with celluloid and other thermoplastic nitrocellulose combinations are given in Vol. V; those of pyroxylin lacquers, waterproofing solutions, bronzing liquids, leather coatings and artificial leathers, in Vol. III.

The analytical examinations detailed in this chapter, are therefore, intended broadly to cover nitrocellulose as such, without especial significance being attached as to the particular technical use to which the product is to be applied.

Detection of the Cellulose Nitrates. Practically all propellent explosives contain or consist of nitrocellulose, either superficially or wholly gelatinized, the majority containing at least 50%, and in the form of nitrated cotton. In admixture the nitrocelluloses may be differentiated from nearly all other nitrogen-containing bodies by the fact that they are insoluble in ethyl alcohol, amyl alcohol, ether, chloroform, carbon tetrachloride or benzene, but are soluble in a mixture of alcohol and ether, methyl, ethyl or amyl acetates, or acetone. Colloided nitrocellulose is recognizable by its hard, tough nature, and horny feel. The various nitrocottons are not quantitatively separable from each other, either by physical or chemical means, nor can they be isolated in a pure state. Nitrogen percentage determinations give but the sum total of nitrogen in the various cellulose nitrates comprizing the mixture under examination.

Ungelatinized nitrocellulose is recognized by the microscopical structure of the cotton filament, combined with solubility determinations, but it must be remembered that cellulose may also be acetated without appreciable change in the physical appearance of the cotton filament, but such esters are distinguished from nitrocellulose by their decreased inflammability and absence of nitrogen.

The differentiation of cotton from nitrated cotton polarimetrically, has already been discussed herein.

Determination of Moisture. A carefully selected, representative sample is taken, quickly rubbed to a fine powder by hand, and pressed through a fine metal sieve. The finely divided sample of nitrocellulose thus obtained is dried on a watch glass, or aluminium or paper tray at a temperature of 45°–55° until constant weight is obtained.

The moisture content will usually fall within the limits of 1%–4.5%. All analytical results are calculated on the basis of the dry substance. The actual time of heating to dry the nitrated cellulose will depend, of course, upon the initial moisture present. With "stove" samples, i. e., nearly dry guncotton direct from the stoves, the moisture content is usually below 1%, and for such the following method of moisture determination is recommended. About 5 gm. of the dried stock is placed in a tared aluminium dish with a tightly fitting aluminium lid. After weighing, the dish and contents are placed in a steam oven (temperature 95°–100°) with the lid removed for one hour. The lid is then replaced, dish and contents cooled in a desiccator for 20 minutes and re-weighed.

According to the U. S. Ordnance method of testing, the moisture in nitrocellulose is determined by spreading 10–100 gm. nitrocellulose evenly out on a paper tray, which is placed in a water oven at 95°–100° and dried, until no further loss in weight takes place.

The nitrated cotton from a Selwig and Lange centrifugal will show 20%–30% of water, that from a hydraulic press 18%–25%, depending upon the fineness of the pulped nitrocotton, and the pressure exerted; while an air-dried nitrocotton will seldom exceed 3%. Guncotton (13% N) as for cordite manufacture, is usually desiccated to a moisture content not exceeding 1%.[1]

N. Hansen[2] has determined the moisture content of nitrocellulose powders of various sizes by drying samples in their normal condition for 3 hours at 80°, then placing them in a magazine for 12 days, and subsequently weighing them daily during the course of a year. Taking the average for the whole of the year, the results show that the amount of moisture absorbed (y) is proportional to the surface of the powder exposed, and can be represented by the equation: $y = \frac{2}{\sqrt{x}}$, where x is the diameter of the grains in millimeters. This law does not hold below a diameter of 0.8 mm., in which case it was found that the amount of moisture absorbed was constant (about 2.1%). The results were obtained with nitrocellulose powders containing 12.7 %–12.8% of nitrogen.

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[1] For the moisture content of nitrocellulose powders, see Vol. VII of this series.

[2] Zts. Schiess. Spreng. 1911, 6, 461; abst. J. S. C. I. 1912, 31, 47;

Determination of Viscosity. As has been stated, the viscosity of a cellulose nitrate solution is an important commercial means of determining as to the particular use to which a given nitrocellulose is best adapted. Uniformity in pyroxylin lacquers, film production and coating compositions are impossible where the viscosity ("flowable qualities") and total solids in the solution are not accurately known. The viscosity of cellulose in cuprammonium solution is also a valuable criterion as indicating the suitability of the material for nitration (see this vol., page 46).

For solutions of low viscosity and containing up to 5 ozs. per gallon of total organic solids, a simple form of viscosimeter is sufficiently accurate to give definite comparable results, the more delicate viscosimeters of Redwood and of Sayboldt being hardly necessary. The principle, however, of allowing a given volume of fluid to pass through an orifice of predetermined diameter at a given temperature, is maintained in all the instruments which have been advocated for this purpose.[1]

For nitrocellulose solutions of low viscosity (thin-flowing mixtures), this constant may be approximately determined by measuring the time required for a standard amount of the solution to flow from the pipette under comparable conditions. R. Fric[2] determined acetone solutions of nitrocellulose and nitro-

C. A. 1912, **6**, 931; Chem. Zentr. 1912, **83**, I, 759; Chem. Ztg. Rep. 1912, **36**, 173; Meyer Jahr. Chem. 1911, **21**, 342.

[1] W. Will, Zts. ang. Chem. 1919, **32**, 133; abst. J. S. C. I. 1919, **38**, 479-A; Ann. Rep. Soc. Chem. Ind. 1919, **4**, 538; Chem. Zentr. 1919, **90**, IV, 99.

[2] Compt. rend. 1912, **154**, 31; abst. J. S. C. I. 1912, **31**, 92; C. A. 1912, **6**, 2531; 1913, **7**, 701 J. C. S. 1912, **102**, i, 73; Bull. Soc. Chim. 1912,

cellulose powders by noting the time required for 25 cc. of the solution to flow through a 2 mm. capillary tube, 20 cm. long.[1]

A 50 cc. glass stopcock burette or separatory funnel with the aperture in the stopcock made quite small, is used for the more fluid solutions, the time required to empty from one mark or graduation to another being recorded. As the results are but comparative, no definite standard has been adopted. Viscosity determinations are usually made in attempts to duplicate given mixtures, or to bring to an arbitrary but definite standard, as regards fluidity, various nitrocotton mixtures. Acetone is taken to dissolve the nitrate, in testing for films and coating compositions, and usually a combination of amyl acetate 65 and benzine 35 parts (by volume) for lacquers. The liquid to be examined is first brought to a definite temperature, usually 25° being taken, a small amount poured into the apparatus and the sides carefully wetted by means of a brush to remove any air bubbles which might adhere and appreciably affect the reading. The viscosimeter is then filled, time given for air bubbles (if any) to rise, and the time for a given volume of liquid to run out of the apparatus, or to fill a receptacle of known capacity placed under the instrument, determined by means of a split-second watch. There are two sources of error in this method. The evaporation of solvent while passing through the air may be sufficient so that duplicate determinations with the same sample are inadvizable, or the solution may be so viscous that a large portion may adhere to the sides of the instrument.

The principle of the Cochius viscosimeter (Fig. 283), consists in measuring the time required for a bubble of air to ascend a certain distance up the tube. The apparatus is filled by opening the stopcock *b*, and pouring in at, *a*, after removing the stopper. The size of the air bubble is determined by the height to which the tube is filled and by the graduations 1, 2, 3, a convenient size bubble being 2 cc. Stopper, *a*, is inserted, cock, *b*, closed, and by turning the stopper the boring is brought opposite the little open-

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11, 820; Chem. Zentr. 1912, **83**, I, 694; Chem. Ztg. 1912, **25**, 149; Meyer Jahr. Chem. 1911, **21**, 341; Zts. Schiess. Spreng. 1912, **7**, 394.

[1] The following comparative results are given (In seconds): Collodion cotton (69.3); after $7^{1}/_{2}$ hours' heating at 80° C. (57.7). Guncotton (210); after $7^{1}/_{4}$ hours' heating at 80° C. (99). French service black powder (36); after 5 hours' heating at 110° C. (21). French sporting powder (94.8); after 12 hours' heating at 110° C. (33.3).

ing in order to relieve any internal pressure. The stopper is then tightly shut, and the apparatus inverted and fastened. The bubble is now just below the stopcock. By quickly turning the cock through 90° it is fully opened, the bubble begins to rise, and by means of a split-second watch the time required for the center of the bubble to pass from *f* to *g* is observed. The number of seconds required for the bubble to pass from one mark to the other may be called the viscosity number. The distance from *f* to *g* is arbitrary, it being evident that the longer the distance the more closely concordant will be the results. From 0.8–1 meter length between *f* and *g* and 100 cc. capacity are convenient dimensions. In the absence of such an instrument a glass tube of about 2 meters in length may be taken, of 40–80 mm. internal diameter, one end being closed, the other stoppered. A mark is made by scratching the glass about 25 mm. from each end. The heavy solution having been reduced to the desired temperature for the observation, is poured into the tube until the latter is nearly full. A small sphere, usually a marble or steel ball from a ball-bearing wheel, is thoroughly rubbed with the solution in order to disentangle the air bubbles that might otherwise cling to the ball, then dropped into the solution in the tube, which is then stoppered. By inverting, the time can be determined of the passage of the ball between the marks on the tube.[1] This apparatus, while apparently crude, is nevertheless susceptible of quite accurate work, and possesses the added advantage of allowing any number of duplicate determinations to be made by simple inversion of the tube.[2]

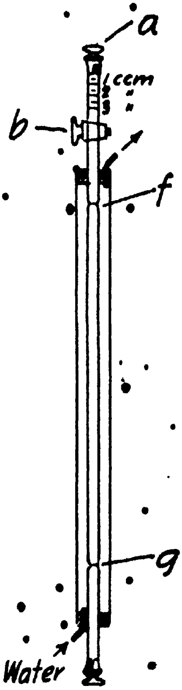

FIG. 283.—COCHIUS VISCOSIMETER

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[1] The accuracy of the temperature of the solution is an important factor. Lunge records an instance where a pyroxylin solution gave a viscosity of 20.35 seconds at 14°, while with a rise in temperature to 25.25°, but 14.18 seconds were required. From this it is seen that viscosity rapidly decreases with increase of temperature.

[2] An alternate method is to use, instead of a ball, a float nearly the

When the viscosities of various types of nitrocelluloses are compared, it is customary to use a series of viscosimeters of this type constructed so that the time of flow may vary. Thus F. Baker[1] has determined the viscosities of nitrocellulose solutions, mostly of concentrations not exceeding 2%,[2] using an apparatus of the above type, of such a construction that the interval measured varied from 100 seconds to 20 minutes. The viscosities of the solutions varied from 0.003 to 40 C. G. S. units. For the standardization of these instruments, water, glycerol and mono-, di- and triacetin were used for comparative measurements, thus avoiding the introduction of short intervals of time.

A modified viscosimeter of the Oswald type has been de-

size of the tube, and used in a manner similar to an Erdmann float in a burette. The speed of motion of the float can be regulated by its diameter, i. e., the more nearly the diameter is to that of the tube, the more slowly will the float ascend.

[1] J. C. S. 1913, **103,** 1653; abst. C. A. 1913, **7,** 4069; J. S. C. I. 1913, **32,** 991; Bull. Soc. Chim. 1913, **14,** 1475; Chem. Zentr. 1913, **84,** II, 1855; Meyer Jahr. Chem. 1913, **23,** 536

[2] The nitrocelluloses used were selected samples of products prepared on a large scale, viz., (a) blasting soluble nitrocellulose, as used in the manufacture of blasting gelatin, 11.85% N, completely soluble in ether-alcohol; (b) highly soluble nitrocellulose, as used in ballistite, 12.38% N, solubility in ether-alcohol, 97.4%; (c) guncotton prepared for the manufacture of cordite, 12.98% N, solubility in ether-alcohol, 96%. The solvents were acetone, ethyl formate, methyl, ethyl, propyl and amyl acetates, ethyl butyrate, acetoethyl-*o*-toluide, ethyl-*o*-tolylethylcarbamate, ethyl phthalate, alcohol-ether, methyl alcohol-ether benzylalcohol-ether, and methyl alcohol-anisole. The methyl-*o*-tolylethylcarbamate (tolylethylurethane) was prepared by the action of ethyl-*o*-toluidine on ethyl chloroformate; it is a colorless oil, boiling at 257° C. at 755 mm. Phenylethylurethane (b. pt. 249° C. at 760 mm.) was prepared in a similar way. Both compounds readily dissolve the "soluble" kinds of nitrocellulose. The viscosities were determined in a series of viscosimeters of the Ostwald-Poiseuille type and the results are given in tables. The variation of viscosity with the concentration of the solution is shown to follow the law: $\eta = \eta_0 (1 + ac)^k$, where η and η_0 are the viscosities of the solution and the solvent respectively, c is the concentration, and a and k are constants depending on the nature both of the solute and the solvent. For comparing different solvents the value of $\frac{d \log \eta}{dc}$ was found most convenient. The variation of this constant with different solvents, using the same nitrocellulose, indicated that the better the solvent the lower the viscosity of the solution. Nitrocelluloses prepared from mercerized cellulose have a much lower viscosity than those from normal cellulose, and the similarity of the viscosities of cuprammonium solutions of mercerized cellulose and normal cellulose respectively, observed by H. Ost (Zts. ang. Chem. 1911, **24,** 1892; abst. J. S. C. I. 1911, **30,** 1247) cannot be due to chemical identity of the two products, as suggested by him, but probably to a change in normal cellulose preceding or accompanying its solution in cuprammonium.

scribed by A. Speedy[1] (see Fig. 284), in which the marks are placed above the surface of the liquid which, therefore, need not be transparent. The apparatus consists essentially of a piece of glass tubing drawn out to form a capillary and bent into U-shape.[2] The constant of the instrument is obtained by calibrating with pure phenol or sulfuric acid.[3]

As the viscosity alters greatly with comparatively small changes in temperature, it is almost imperative to have the viscosimeter immersed in some form of thermostat during the reduction of

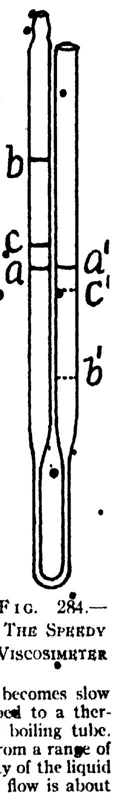

Fig. 284.—The Speedy Viscosimeter

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[1] J. S. C. I. 1915, **34**, 597; abst C. A. 1915, **9**, 2166; J. C. S. 1915, **108**, ii, 549

[2] The liquid, the viscosity of which is to be determined, is filtered into the viscosimeter, which is clamped vertically in the bath so that the level marks *aa'* are just above the surface of the heating liquid. The bath is then heated to the required temperature and after a few minutes the levels *aa'* are carefully adjusted. By means of a piece of rubber tubing the liquid is then slowly sucked up the left limb of the tube until it passes the level *b*. It is then allowed to descend; the time taken to fall from *b* to *c* is recorded. Part of the liquid under observation is above the surface of the heating liquid and is, therefore, at a slightly lower temperature, but as the level falls, this part of the liquid regains its former temperature. The error due to unequal viscosity in different regions arising in this way is negligible, as it is only the viscosity of the liquid in capillary tube that counts. The thinness of the wall of the capillary tube ensures that the liquid passing through the tube is at the temperature of the bath. The column of liquid, *bc*, never reaches the capillary. The level *b'* is well above the point where the constriction in the right limb of the tube begins. The time of flow from *b* to *c* only, is taken because on approaching *a* the motion becomes slow and uncertain. The instrument may conveniently be strapped to a thermometer and suspended in the heating liquid contained in a boiling tube. The cheapness of the apparatus renders it possible to choose from a range of tubes one with a capillary of diameter best suited to the viscosity of the liquid to be examined. The best results are obtained if the time of flow is about 1–2 minutes at the temperature of observation. Results are reported on 6 oils using the above instrument, the totally immersed type of Dunstan and the Redwood form. The readings of the first 2 instruments agree within the limits of experimental error. At 60° Redwood seconds may be obtained approximately by multiplying these readings by 500.

[3] A. Dunstan and H. Langton, Proc. Chem. Soc. **28**, 14; J. C. S. 1912, **101**, 418; abst. C. A. 1912, **6**, 1702; Bull. Soc. Chim. 1912, **12**, 1090; Chem. Zentr. 1912, **83**, I, 1688. A. Dunstan, Proc. Chem. Soc. 1914, **30**, 104; abst. C. A. 1915, **9**, 405. Cf. A. Dunstan and R. Wilson, J. C. S. 1907, **91**, 85; abst. C. A. 1907, **1**, 956; Chem. News, 1906, **94**, 303; Bull. Soc. Chim. 1907, **2**, 1153; Rep. Chim. 1907, **7**, 194; Chem. Zentr. 1907, **78**, I, 1009. See also R. Kremann and R. Erlich, Monatsh. 1907, **28**, 831.

the dissolved nitrocellulose solution to the desired temperature.[1]

The viscosimeter of H. Ost (see p. 46) is intended primarily for the determination of cellulose when dissolved in cuprammonium solutions. H. Barthelemy[2] measures viscosity by means of the "ball method," i. e., the time taken for a nickel ball 5 mm. diameter to fall through 50 cc. of solution contained in a glass tube 3 cm. in diameter. The time in seconds taken is recorded as the viscosity.

The consistency apparatus of Stahl[3] indicates the number of seconds which an air-bubble of fixed volume is required to pass from the bottom to the top of a glass cylinder or tube of fixed height, filled with the test sample at 17.5°. A comparison with a normal or standardized sample in the same instrument at the identical temperature determines the suitability of the ester in solution for the purpose intended.

According to the law of G. Stokes the velocity of a falling body in a solution is inversely proportional to the viscosity coefficient of the solution, and in consequence, the time of the fall of a sphere through a definite depth of liquid is directly proportional to the viscosity of that liquid. A simple form of apparatus used by H. Wolff[4] for the determination of viscosity depends in principle on Stoke's law. The time in which a spherical or spindle-shaped body takes in falling from the top to bottom of a tube (or from one mark to another on the tube), at a constant temperature gives a figure from which the relative viscosity of the solution may be estimated, when comparative experiments under similar conditions are made with other liquids.

For unusually viscous liquids—those beyond the range of the ordinary viscosimeter—other types of apparatus have been devized. An approximate test is made by placing the nitrocellulose in a long glass-stoppered cylinder, and comparing the time required for the solution to flow from one end to the other when the cylinder is inverted, against a similar sized sample of the standard solution, both being tilted in the same manner together. This method is often used in judging of the fitness of dopes for pyroxylin artificial leather manufacture.

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[1] W. Ray and J. Reilly, Chem. News, 1918, **117**, 181; abst. C. A. 1918, **12**, 1429. L. Meggitt, J. S. C. I. 1902, **21**, 106; abst. Chem. Centr. 1902, **73**, I, 602.

[2] Caout. et Guttap. 1913, **10**, 7202; abst. C. A. 1914, **8**, 243; Mon. Sci. 1913, **78**, 549; Chem. Zentr. 1913, **84**, II, 1617.

[3] L. Andes, Rev. Fett-Harz-Ind. 1907, **14**, 76; abst. C. A. 1907, **1**, 1909; Chem. Zentr. 1907, **78**, I, 1464; Wag. Jahr. 1907, **53**, II, 551.

[4] Farben Ztg. 1912, **17**, 2108; abst. C. A. 1912, **6**, 3192; Chem. Ztg. Rep. 1912, **36**, 508.

T. Chandelon[1] having observed that the viscosities of 4.5% collodions differ according to whether the nitrating mixture contained 15% or 20% of nitric acid, investigated this difference with higher concentrations.[2] For highly viscous liquids, the viscosities may also be compared[3] by noting the time required for a glass sphere (7-8 gm. weight) to fall through 20 cm. columns of the liquids under fixed conditions.

In the Stormer viscosimeter the comparative viscosity is obtained by measuring the number of revolutions that a paddle makes in the solution under standard conditions. 50 cc. of the liquid are placed in the cup of the viscosimeter instrument and a paddle just immersed in the liquid and the temperature adjusted to 21°. The apparatus is so constructed that it is a simple operation to compare accurately the times required for the paddle to make a given number of revolutions or to measure the number of revolutions made in the same length of time. When worked in samples of high viscosity it is advized to note the time required to make 100 revolutions. All calculations are based on the water unit and the driving wheel may be adjusted with shot so that one hundred revolutions are given in about twelve seconds.

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[1] Bull. Soc. Chim. Belg. 1914, **28**, 24; abst. J. S. C. I. 1914, **33**, 222; C. A. 1914, **8**, 1506; Chem. Zentr. 1914, **85**, II, 1315; Meyer Jahr. Chem. 1914, **24**, 424; Wag. Jahr. 1914, **60**, I, 358; Zts. ang. Chem. 1914, **27**, II, 503.

[2] The material was specially prepared, and the Cochius' viscometer used for the determination. It was found that the 5% collodion made with nitrocellulose from the 20% bath gave a viscosity equal to that of a 5.74% collodion from the 15% bath, and that this ratio (1.33), called the coefficient of viscosity, was maintained up to about an 8% collodion. Mixtures of 1 to 2 and of 3 to 2 alcohol-ether gave collodions of about equal viscosity from equal percentages of a nitrocellulose. A commercial nitrocellulose was found to have a coefficient of 0.62. From the coefficient the quantity of solvent to give a required viscosity may be calculated. For collodions so viscous as to be above the range of the viscometer, an instrument was constructed by means of which the extensibility (viscosity) was measured as the distance at which a film of the collodion drawn out between two discs was just ruptured. From experiments on solutions containing from 12.82% to 19.3% of nitrocellulose, the coefficient was found to be 1.41. Hence, although the use of a nitrating mixture containing 15% nitric acid involves a loss of 11% in yield, the resulting nitrocellulose requires only 1 part of solvent where a nitrocellulose made with a 20% mixture, without loss, would require from 1.33 to 1.41 parts.

[3] H. Schwarz, Zts. Chem. Ind. Koll. **12**, 32; abst. J. S. C. I. 1913, **32**, 191; C. A. 1913, **7**, 2304; J. C. S. 1913, **104**, ii, 189; Chem. Zentr. 1913, **84**, II, 163; Wag. Jahr. 1913, **59**, II, 593; Zts. ang. Chem. 1913, **26**, II, 406.

In the direct-reading viscosimeter of R. MacMichael[1] a disc is suspended in the fluid under examination by means of a torsion wire, about 10 in. long, which passes through the stem of a plunger and is fastened near the bottom, the triangular head of the wire being held between grooved pins on a standard. The plunger is provided with a dash-pot to check vibration and damp the action, and carries at the top a graduated dial. The fluid is contained in a double-walled cup of heavy spun brass, the space between the walls serving as a heating jacket and being provided with an electric heating coil. The cup is rotated by an electric motor and the deflection of the disc noted by means of a pointer on the standard. The instrument is calibrated by means of sugar syrup, and the viscosity is then read directly from the indication of the dial. It can be used for determining the viscosity of clay slips and of solutions of glue, gum, starch, gelatin, etc.; straining is not necessary, as small particles of solid matter do not affect the accuracy of the determination.

The viscosity apparatus of L. Gümbel,[2] E. Kafka,[3] W. Stone,[4] G. Sayboldt[5] and F. Lidstone[6] are applicable to nitrocellulose solutions, and in general, embrace the same features as the instruments just described.

Viscosity by Ostwald Viscosimeter. The Ostwald modification of Poiseuville's apparatus for the determination of the viscosity of dilute solutions—either nitrocellulose or cellulose acetate—is shown in Fig. 285, and consists of a capillary tube *DB* (about 10 cm. long the bore varying according to the viscosity of the liquid being tested) through which a definite column of liquid—i. e., that contained between the marks *C* and *D*—is allowed to flow under the force of its own weight. A definite volume of

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1. R. MacMichael, J. Ind. Eng. Chem. 1915, **7,** 961; abst. J. S. C. I. 1915, **34,** 1226; C. A. 1916, **10,** 135.
2. D. R. P. 283732, 1914; abst. Kunst. 1915, **5,** 84; Chem. Zentr. 1915, **86,** I, 1035; Chem. Ztg. Rep. 1915, **39,** 183; Wag. Jahr. 1915, **61,** I, 465; Zts. ang. Chem. 1915, **28,** 273.
3. Aust. P. 6441, 1913; abst. C. A. 1914, **8,** 2509.
4. Engineering, 1915, **100,** 554; J. S. C. I. 1915, **34,** 1274.
5. U. S. P. 1132621, 1915; abst. J. S. C. I. 1915, **34,** 515; C. A. 1915, **9,** 1137.
6. J. S. C. I. 1917, **36,** 270; 1918, **37,** 148-T; abst. C. A. 1917, **11,** 1575; 1918, **12,** 1713; J. C. S. 1918, **114,** ii, 221; Chem. Zentr. 1917, **88,** II, 261; 1919, **90,** II, 634; Ann. Rep. Soc. Chem. Ind. 1917, **2,** 76, 336; 1918, **3,** 70.

liquid is introduced into the larger bulb E through the tube F by means of an accurately calibrated pipette, and is then, either by blowing through, F, or by sucking at, A, forced up through the capillary until the level of the liquid rises above the upper mark C. The liquid is then allowed to flow back through the capillary, and the time required for the surface of the liquid to pass from, the mark C to the mark D is noted.

Before being used, the viscosity tube is thoroughly cleaned so that there are no obstructions in the capillary, and the liquid runs clean from the glass without leaving drops behind. To secure this, the instrument is filled for some hours with a warm solution of chromic acid and then thoroughly washed with distilled water, which is drawn through the tube with the aid of a filter pump. The tube is then dried by washing successively with alcohol and ether, removing the latter by means of a current of (preferably warm) air.

As the viscosity of a liquid varies greatly with the temperature (roughly 2% per degree), the tube and liquid must be kept at a constant temperature during the measurement. The tube, therefore, is suspended in a bath, the temperature of which can be regulated to within 0.1°. The sides of the bath are constructed of glass to permit observations of the time of flow, and stirring is accomplished by means of a current of air from a compressed air main.

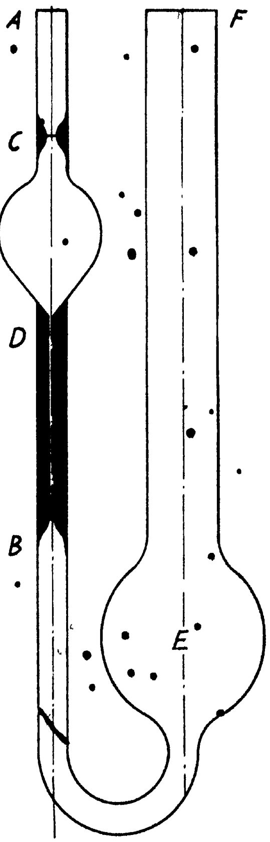

Fig. 285.—Ostwald Viscosimeter

Five cc. of the solution being tested are introduced into the bulb E by means of a calibrated pipette. The tube is then fixed in a perpendicular position in the bath, and is immersed at such a depth in the water of the bath that the upper mark C is well beneath the surface. After allowing 10–15 minutes for the temperature of the tube and liquid to become constant, a piece of rubber tubing is attached to the narrower limb of the viscosity tube, and the liquid is sucked up to above the mark G. If the liquid is very viscous this operation is varied, and the liquid is forced up by means of compressed air applied to the wider limb F.

The liquid is then allowed to flow back through the capillary, and a stop watch started as the meniscus passes the upper mark C, and stopped again as the meniscus passes the lower mark D. The measurement is repeated four or five times, and the mean of the determinations taken. Greater deviations than 0.1%–0.3% from the mean value point to the capillary tube being dirty, or to the liquid containing particles of suspended matter.

The viscosity of the liquid being tested, relative to that of any standard liquid, is calculated by means of the formula:

$$\frac{t \times D}{t_1 \times d_1}$$

where t is the time of flow of liquid; D the density; t_1 the time of flow of the standard; and d_1 the density of the standard.

The coefficient of viscosity in absolute units may be calculated by means of the formula:

$$\frac{11\,pr\,4t}{8\,Vl}$$

where p is the driving force; r the radius of the capillary; t the time of flow; V the volume passing through capillary; and l length of capillary. It is easier, however, to obtain the coefficient of viscosity in absolute units by choosing as a standard a liquid in which the coefficient of viscosity is known, and substituting in the following equation the value of N_1 in absolute units:

$$\frac{n}{n_1} = \frac{t \times D}{t_1 \times D_1}$$

where n is the absolute viscosity of the liquid under examination; n_1 is the absolute viscosity at the temperature of the experiment of the standard liquid, and the remaining values as in the first equation above.

Water is often conveniently chosen as a standard, and the following values may be used in calculating the coefficient of viscosity in absolute units: Temperature, 0°, 0.01793; 10°, 0.01311; 20°, 0.01006; 30°, 0.00800; 40°, 0.00657; and at 60°, 0.00550.

Viscosity by the "Ball Fall" Method. The English Government, it is understood, as the result of investigation of the various methods which have been proposed for viscosity determinations of nitrocellulose solutions, have adopted the "falling ball" method, previously alluded to. This method consists in determining the time taken for a steel ball to fall a fixed distance through the solution under examination. It was shown by Stokes in 1850 that a small sphere falling in a liquid soon assumes a constant velocity, which is represented by the formula:

$$\frac{v - 22r(S - S')g}{9N}$$

where r is the radius of the sphere; S the specific gravity of the sphere; S' the specific gravity of the solution; N the viscosity coefficient of the solution; g the gravity constant; and v the velocity of the sphere. When Stoke's equation is rigidly obeyed the velocity is inversely proportional to the viscosity coefficient, and hence the time of fall of the sphere is directly proportional to the viscosity coefficient.

In the apparatus shown in Fig. 286, irrespective of how closely Stoke's equation is obeyed in the practical apparatus shown, it is obvious that for practical purposes the time obtained in this apparatus should give relative indications of the viscosity of different nitrocellulose solutions. In order to obtain results of maximum consistency in carrying out the determination, the following are important points to bear in mind:

(a) The temperature of the solution must be kept constant.

(b) The balls used must be uniform in size and density.

(c) The balls must attain a constant velocity before measurement begins.

(d) The ball must drop without fouling the walls of the containing vessel.

(e) The ball must be free from adhering air bubbles.

(f) The tubes used must all be of uniform diameter.

The solvent employed comprizes 1.5 volumes ether (sp. gr.

0.72) and 1 vol. alcohol (sp. gr. 0.817 or 92% by weight). The sample of nitrocellulose to be tested is first freed from any excess of water by pressing between filter papers and dried, 1–1.5 hours in a steam oven being sufficient. After the dried sample has cooled in a desiccator, 10 gm. are weighed out on an aluminium scoop and transferred to the flask. 100 cc. alcohol are added, and the nitric ester thoroughly wetted by shaking, after which 150 cc. ether are poured in. The flask is then stoppered and vigorously shaken by hand to prevent the agglutination of the nitrocotton into lumps. It is then shaken at intervals until solution is complete. It is advizable to leave the solution overnight.

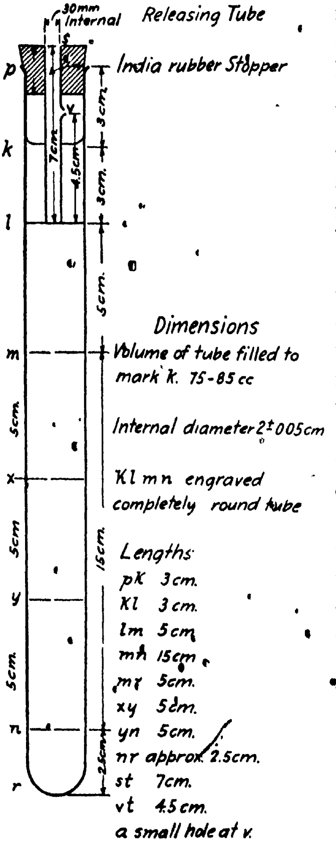

Fig. 286.—Viscosity Determination by the "Ball Fall" Method

Before proceeding with the test it is advizable to examine the solution in the flask in order to detect the presence of translucent partially colloided particles which might interfere with the flow of the solution. Agitation, of course, must be continued until solution is complete. As the viscosity of the solution to some extent is influenced by light, undue exposure to bright light should be avoided.

In manipulating the test, the apparatus is placed in position and leveled, after which the viscosimeter is filled to the mark *k* with castor oil andt he releasing tube inserted, the end of this tube being adjusted to the level of the mark *l* on the tube. Care should be taken that it is centrally situated throughout its length. The water jacket is then brought to 20°, ±0.3°, and should be maintained at this temperature. It is also desirable to adjust the room temperature to about 20°. The tube is placed in position in the water jacket and allowed to attain the temperature of the bath. One of the steel balls is then inserted in the releasing tube, it slowly travels down through the liquid in the releasing tube and should free itself from air bubbles in doing so.

When the ball passes the mark *m* the stop watch is started, and when it passes the mark *n* it is stopped. If the ball fouls the sides of the tube the result is rejected. The time of fall for castor oil should be 17-18 seconds.

In determining the viscosity of the nitrocellulose solution, a viscosimeter tube is filled to the mark *k* with nitrocotton solution from a flask, care being taken to avoid as far as possible, the introduction of air bubbles. The releasing tube is inserted and the determination carried out as described above. The time of fall may be measured between *mx*, *my* or *mn*, according to the viscosity of the solution being tested. The results are recorded as the time of fall in seconds, and the time of fall with castor oil also quoted as a check on the results.

Determination of Solubility. The degree of solubility of a cellulose nitrate in a specified liquid or series of solvents should always be determined in advance, in order to judge if the pyroxylin is satisfactory for the use intended. This is especially important in the manufacture of photographic films, and in the formation of artificial filaments, for with the former the small specks of undissolved product show up as distinct particles in the developed negative or film, and when these are magnified as in "moving pictures," they give either a continued blurred appearance or a succession of light patches flitting across the screen. With filaments, the fine specks of undissolved portions soon clog the spinning orifices and interrupt the continuity of the thread.

One method of determining the solubility is to dissolve 5 gm. of the air-dry sample in 100 cc. of the particular solvent mixture that the cellulose nitrate is to be used in commercially,[1] or if the viscosity is high, the solvent may be increased to 200 cc. The glass-stoppered flask is shaken frequently to facilitate solution, either alone or after the introduction of a weighed amount of shot or glass beads,[1] until all that will dissolve has gone into solution. Allow to stand at rest for four hours, or until the sediment has deposited, then decant carefully the supernatant liquid without disturbing the precipitate. Add 100 cc. solvent to the contents of the flask, shake vigorously and filter the precipitate through a Gooch crucible or tared filter paper, dry at 100°, and subtract the weight of the shot or beads, the difference being the weight of insoluble material in the sample taken. Usually 1-1.5 hours' drying is sufficient. Where quick and approximate determinations are to be made a portion of the 5% solution is placed in a 10 cc. urinary tube graduated in $^1/_{10}$ cc. and rotated for fifteen minutes at the highest speed. The precipitate may now be easily read off, and results obtained in this manner, in the author's hands, have proven quite satisfactory.[2]

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[1] The particular solvent intended to be used on the factory scale should always be taken, on account of the varying results obtained with different solvents. A pyroxylin which gives a certain percentage of undissolved residue in ether-alcohol will not necessarily give the same amount when the solvent is changed to, say, amyl acetate-benzine (60%-40%).

The official English method of determining solubility, which is employed primarily with "high nitrogen" nitrocellulose of 13%-13.2% N, is as follows: 3.24 gm. (50 grains) of the nitrocellulose are placed in a cylinder of 230 cc. capacity and covered with 200 cc. of ether-alcohol (2 parts ether, sp. gr. 0.72, and 1 part alcohol, 60° over proof) and the cylinder placed in a mechanical shaker for one hour, or digested at 15.5° for 6 hours with frequent shaking (at 15-minute intervals). The contents of the cylindor are then allowed to settle and an aliquot portion of the clear solution then removed, evaporated to dryness in a weighed dish at 50°, and then weighed. From the weight of soluble nitrocellulose found, the percentage of this present in the original sample is calculated In a modification of this method sometimes employed, the alcohol is first added to the nitrocellulose and thoroughly mixed, after which the ether is poured in. A second portion of the supernatant liquid as a check, may be precipitated with chloroform and filtered through a tared filter paper.

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[1] In order to affect solution more quickly by disintegrating the viscous gelatinized nitrated cellulose.

[2] A method of solubility determination often used, is to dissolve out the solvent portion and evaporate to dryness the solvent containing the nitrocotton in solution. This method gives uniformly high results, due to the difficulty of removing the last traces of solvent, an entirely soluble nitrate often giving—apparently—102%-104%.

The precipitate is redissolved in ether-alcohol, reprecipitated by chloroform, dried and weighed.

In the method as devized by H. Mallinson,[1] 5 gm. of the guncotton (or 2 gm. if the amount of soluble nitrocellulose is known to be 25% or higher) is treated with 200 cc. of ether-alcohol in a graduated cylinder, which is then shaken mechanically for about 1 hour. After allowing to settle, 50 cc. of the supernatant liquid is transferred to a porcelain dish and treated with 500 cc. of water at about 75°-80° C. The precipitated nitrocellulose is submerged by means of a glass rod to expel the last traces of solvent, and if it forms a coherent mass, it is transferred to a piece of filter-paper resting on absorbent material, moistened with alcohol, partially dried by pressing between filter paper, and then completely dried in an oven at 160° F. (70° C.). If the precipitate is not coherent, it is collected on a double filter, of which one paper has been counterpoised against the other, or in a tared Gooch crucible. The method is much quicker than the British Government process in which a known volume of the ether-alcohol solution is evaporated, and it gives somewhat lower and more accurate results, since it is very difficult to remove the last traces of solvent by evaporation.

In addition to the difficulty of completely removing the residual solvent from the extracted nitrocellulose and in the drying of the colloidal material, there is also a difficulty in obtaining comparable results when ether from different sources is employed. Commercial methylated ether usually contains appreciable amounts of both di-methyl and ethylmethyl ether and these substances have solvent action to different degrees from that of diethyl ether on various nitrocelluloses.

The official United States method for the determination of nitrocellulose "soluble" is different from the above method. Instead of weighing the soluble, direct determinations are made of the insoluble and the unnitrated cotton. The "soluble" is obtained by difference. For the solubility determination, a small quantity of the finely-sifted cellulose nitrate (0.5-1 gram) is treated with a mixture of 350 cc. of pure ethyl alcohol and pure ether (ethyl) (sp. gr. o.748-o.750 at 20°) in a stoppered vessel. The vessel is placed in a mechanical shaker for $^1/_2$–1 hour, after which its contents are allowed to settle. The clear liquid is siphoned off and the extraction process then repeated a second time. The insoluble portion is collected on a Gooch crucible in the usual way and washed with further quantities of ether-alcohol mixture. The residue is partly dried at 80° and then at 100° to constant weight.

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[1] J. Ind. Eng. Chem. 1916, **8**, 401; abst. J. S. C. I. 1916, **35**, 706; C. A. 1916, **10**, 2524; J. C. S. 1916, **110**, ii, 400.

In the official German method a quantity, weighing 2 grams, of the finely divided dry cellulose nitrate is placed in a 500 cc. stoppered vessel, 215 cc. of ethyl alcohol (sp. gr. 816 at 50°) are added and the material well wetted; 285 cc. of pure ether (sp. gr. 0.720) are then added and the vessel shaken for 5 hours, after which the contents of the vessel are allowed to settle. 250 cc. of the clear liquor are removed, 10 cc. water added and the mixture evaporated on the water bath. The residue is finally dried at 80° for $^1/_2$ hour and then weighed.

In the method for the estimation of soluble nitrocellulose as recommended by K. Quinan,[1] about one gm. of the finely divided dry sample to be analyzed is placed in an aluminium cup 1.9 in. in diameter and $4^1/_8$ in. deep. It is covered and well stirred with 50 cc. of alcohol, 100 cc. of ether are then added, and the mixture is stirred for several minutes. After removing the stirrer the cup is lightly covered with an aluminium lid, and is then placed in the steel cup of a centrifugal machine, which is gradually raised to a speed of 2000 revolutions per minute, the total centrifugal force at the position occupied by the cups (which become horizontal when in rapid rotation) is about 450 lbs. They are rotated at the full speed for 10–12 minutes, and the machine is then gradually stopped. By this time the whole of the insoluble matter will be at the bottom of the cup, and the supernatant solution will be clear; it is drawn off to within a quarter of an inch of the bottom without disturbing the sediment), with the aid of a vacuum pipette. Care must be taken that the solution thus withdrawn is perfectly clear. About 10–15 cc. of colloid solution and a film of insoluble matter remain at the bottom of the cup; these are stirred up well, the stirrer is rinsed with ether-alcohol, about 50–75 cc. of fresh ether-alcohol are added; the mixture is again treated in the centrifugal apparatus for about eight minutes; the whole washing process is then repeated until all soluble matter has been removed. This may require about seven or eight (or for samples with much insoluble matter 10 or 12 or more) washings, but as the extraction proceeds, the period of rotation may be somewhat reduced. After extraction is completed, the insoluble matter is transferred to a Gooch crucible with the usual asbestos pad, dried at 100° C. and weighed. The residue may, if wished, be dried and weighed in the aluminium cup, but then it cannot be ignited. The entire time for an analysis, exclusive of that required for drying, is from one to two hours, the average time being $1^1/_4$ hours. The results are satisfactory, both as to accuracy and rapidity. The centrifugal apparatus used is sketched and minutely described; it is provided with two arms, so that two tests may be made simultaneously. Acetone-soluble nitrocellulose may be determined by the same method. Care must, of course, be taken that the solvents employed are free from all matter not volatile at 100°.

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[1] J. A. C. S. 1901, **23**, 258; abst. J. S. C. I. 1901, **20**, 845; Chem. Centr. 1901, **72**, II, 147; Jahr. Chem. 1901, **54**, 896; J. C. S. 1901, **80**, ii, 480; Rep. Chim. 1901, **1**, 449.

An extensive study of the solvent action of "alcohol-ether" mixtures on nitrocellulose has been made by A. Matteoschat.[1] In the case of completely soluble nitrocellulose the proportion of ether to alcohol may be widely varied without altering the solubility figure. This conclusion confirms the results of other workers. Thus a nitrocellulose containing 11.5% of nitrogen was found by G. Lunge and J. Bebie[2] to be completely and easily soluble in mixtures of ether-alcohol in the ratio 3: 1 as well as 6: 1, while in a mixture of 9 parts of ether and 1 part of alcohol the solubility was 95%. With increase in the proportion of ether the solubility fell. Thus, when a mixture containing 27 parts ether and 1 part of alcohol was used, a solubility of 7.3% resulted. In the solubility determination of the incompletely soluble nitrocellulose, both the ratio of ether to alcohol as well as the concentration of the latter, play important parts. A. Matteoschat determines the solubility by treating 5 grams of the cellulose nitrate in a stoppered cylinder with a definite amount of alcohol and then adds sufficient ether to make the solution up to 500 cc. After shaking for one hour, the contents of the cylinder are allowed to settle overnight. The cylinder is again shaken and then set aside for 46 hours. 100 cc. of the clear liquor are transferred to a weighed Erlenmeyer flask and then evaporated to dryness on the water bath. The residue receives a final drying for 24 hours at 30°. Adding the two solvents separately gives higher results than when mixed solvents are added direct to the nitrocellulose, e. g., 40.5% compared with 32.2%. The conclusions from this work are summarized as follows:

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[1] Zts. Scheiss. Spreng. 1914, **9**, 105; abst. Chem Zentr. 1914, **85**, I, 2095; J. C. S. 1914, **106**, i, 1166; C. A. 1914, **8**, 1669; Meyer Jahr. Chem. 1914, **24**, 304; Zts. ang. Chem. 1914, **27**, II, 730.

[2] Zts. ang. Chem. 1901, **14**, 483, 507, 537; J. A C. S. 1901, **23**, 527-578; abst. J. S. C. I. 1901, **20**, 1021; Rep. Chim 1901, **1**, 494; Chem. Centr. 1901, **72**, II, 34, 92, 764; Jahr. Chem. 1901, **54**, 893; Meyer Jahr. Chem. 1901, **11**, 316; Wag. Jahr. 1901, **47**, I, 495. See also Zts. ang. Chem. 1899, **12**, 441, 467; abst. Chem. Centr. 1899, **70**, I, 1272.

(1) The difference in the solubility at different volume relations of the same components of the solvent mixture within relatively small limit of 1:1 and 3:1, (14.2%-57.5%, or a difference of 43.3%); and also by the use of different concentrations of alcohol in the same ratio mixtures, is considerable. The greatest difference is in a 1:1 mixture, with 99.5% alcohol it is 52.3%; with 80% 14.2%; or a difference of 38.1%.

(2) The mixture ratio of 1:1 is only favorable when alcohol of the highest concentration is employed (99.5%); with technical alcohol better results are obtained with a 2:1 and 3:1 mixture.

(3) When it is necessary to dissolve nitrocellulose in ether-alcohol, it is recommended that the alcohol be added first and the other added later with thorough agitation, and after the alcohol has had opportunity to thoroughly saturate the nitrocellulose. The direct use of the ether-alcohol mixture decreases the solubility.

(4) 99.5% alcohol gives, when used in the ratio of 1:1, a solubility of 52.3%, at a ratio 2:1, 40.5% or 11.8% less; and at 3:1 only 25% or 27.3% less. Herewith the opinion which Schwalbe, as well as Lunge and Bebie hold, namely, that decrease in alcohol decreases the solubility of nitrocellulose in ether-alcohol, is verified; that is in so far as highly concentrated alcohol is concerned. Yet the increase of the alcohol above the 1:1 ratio does not increase the solubility, but causes it to fall to 34.4% for 1 part of ether and 2 parts of alcohol, where 1:1 gives 52.3%. Weaker alcohol yields the best results (highest solubility) when the mixture contains more ether than alcohol.

(5) T. Chandelon's opinion[1] is verified, namely, that water-free ether-alcohol dissolves guncotton better than the hydrous mixture, but only on condition that the ether represents the greater constituent, for in the 1:1 mixture the solubility sinks with increasing hydration of the mixture from 52.3% to 14.2%.

(6) The view put forward by the author (Worden) that the solvent action of ethyl alcohol on guncotton decreases with increasing water-content is verified not only for low, but also for high nitrated celluloses. Alcohol-water mixture plus ether increases the solubility.

(7) In all solubility determinations of nitrocellulose in ether-alcohol it is imperative to state the mixture ratio and the percentage of the alcohol used, as well as to state whether the mixture was employed, or if the alcohol were added first, and then, after shaking, the ether.

The solubility figures of various nitrated celluloses depend, among other factors, on the purity of the solvent, and on the relative proportions of the constituents of the mixture. The solubility figure is also influenced by the previous treatment of the cellulose and also by the method of preparation and purification of the nitrocellulose. Thus the strength and composition of the mixed acids and the temperature and duration of nitration process all show their effects. The type and extent of the purification process also influence the solubility figure.

A. Schrimpff[2] determines the solubility as follows: 2 gm. of nitrocellulose after drying over sulfuric acid in a vacuum desiccator, is transferred to a cylinder containing about 100 cc. of ether-alcohol (ether, sp. gr. 0.72, 2 parts; alcohol, 95%-96%, 1 part), and rinsed in with a further 100 cc. After periodical shaking for 6 hours, the nitrocellulose is allowed to settle, and 100 cc. of the clear, supernatant liquid withdrawn into a glass dish and evaporated on a water bath until the residue assumes a horny appearance, at which stage the drying is completed in a steam oven. He emphasizes the fact that solubility in ether-alcohol is influenced by factors such as the strength of the alcohol and the manner in which the solvents are added.

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[1] Bull. Soc. Chim. Belg. 1912, **26**, 495; Kunst. 1913, **3**, 69; C. A. 1913, **7**, 1418; J. S. C. I. 1912, **31**, 1202; J. C. S. 1913, **104**, i, 18; Chem. Centr. 1913, **84**, I, 392; Zts. ang. Chem. 1913, **26**, I, 268, 366. Bull. Soc. Chim. Belg. 1914, **28**, 13; J. S. C. I. 1914, **33**, 222; Kunst. 1914, **4**, 4, 25; C. A. 1914, **8**, 1009, 1506.

[2] Zts. Schiess. Spreng. 1920, **15**, 17, 38, 53; abst. J. S. C. I. 1920, **39**, 314-A.

Determination of Insoluble Nitrocellulose. The statement is found in the literature that all forms of cellulose nitrate are soluble in acetone and acetic ether, and a rough method of estimating unchanged cellulose has been suggested by dissolving the cellulose nitrate in one of these solvents, the insoluble portion being cellulose. In many examinations of ethyl acetate-insoluble residues from cotton nitration, the author has yet to find one free from nitrogen, even after the acetate has been left in contact with the nitrated cotton for periods of as long as two weeks, with daily change of solvent. The percentage of nitrogen as calculated on the sample dried at 100° has varied from 0.2–4.7, thus indicating the presence of nitrogen-containing bodies in nitrocotton, insoluble in ethyl acetate. The anomalous results in solubility reported by different investigators render accurate generalizations impossible at the present time. A nitrocotton of 12.5% nitrogen may be practically insoluble in ether-alcohol or may entirely dissolve to a clear and fluid solution.

The acetone insoluble may be determined as follows: One gram of the finely divided dry nitrocellulose is placed in a long, stoppered tube and 250–300 cc. acetone added; the bottom of the tube is constricted to one-half inch in diameter, cylindrical shape and graduated (the graduations have been made from a series of direct determinations of residues). The tube containing the nitrocellulose and solvents is thoroughly shaken and then allowed to settle until the supernatant liquor is clear (i. e., about 24 hours). The volume of settled residue—called the "volumetric reading" is carefully noted and compared with the volume occupied by the residue from one gram of standard nitrocellulose, the residue from which is small and has been previously determined gravimetrically; if the volumetric reading is 0.2% or less, it is thought that the difference between volumetric and gravimetric results is not greater than the limit of error of the operation, and the volumetric reading is considered to be the true result. If greater than 0.2%, the determination is made gravimetrically as follows: The supernatant liquid is siphoned off, down to within about $^1/_4$ inch from the upper surface of the residue, the tube is refilled with acetone, accompanied by vigorous shaking, allowed to settle at least 16 hours, and the liquid siphoned off as before. These decantations are continued until a total of from three to five (depending on the amount of residue) have been carried out. After the last decantation the residue is transferred to a small beaker, by aid of a long, glass rod and fresh acetone for rinsing, then filtered through an asbestos filter tube, consisting of a large test tube with its lower end drawn to a blunt point and terminating in a hole of about $^1/_8$" diameter; the lower end of the tube contains a mat of shredded asbestos which has been previously heated to a red heat for several minutes. After the residue on the mat has been washed until portions of the evaporated filtrate shows no soluble material the tube and contents are dried at 13° ± 3° until all odor of acetone has disappeared, then dried to constant weight at 95° 100° C., cooled and weighed again and the loss of weight gives the "insoluble in acetone."

In the method of A. Schrimpff,[1] foreign matter and unnitrated cellulose are determined by treating 5 gm. with 125 cc of a clear, aqueous solution of sodium sulfide (200 gm. in 800 cc.) in a porcelain dish, and gently boiling for 10 minutes. The residue is washed with water on a dry, tared linen filter previously treated with sodium sulfide, HCl and water, and dried. The weight of the residue gives the foreign matter, from which the unnitrated cellulose is calculated by deducting the ash.

Unaltered Cellulose may be estimated by boiling a small sample with sodium stannite[2] solution, carefully washing out the stannite with warm water and drying. The cellulose nitrates are dissolved by this treatment, leaving the unchanged cellulose as the residue. Or a weighed sample of the ester is shaken with ether-alcohol until no more dissolves, filtered, and the residue shaken with ethyl acetate and acetone until no more passes into solution. The ether-alcohol dissolves the lower nitrates and the ethyl acetate and acetone the higher nitrates, the undissolved residue being unchanged cellulose. The unconverted cotton may also be determined by boiling a fresh quantity of the air-dry sample (usually 5 gm.) with a saturated aqueous solution of sodium sulfide. After allowing to stand at a temperature of 40°–60° for two or three hours the mass is decanted or filtered, and the process repeated in the same way. The insoluble residue, which consists of unnitrated cellulose, is first washed with dilute HCl, then water, dried and weighed. In more accurate work the cellulose is finally ignited and the weight of the ash deducted.[1]

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[1] Zts. Schiess. Spreng. 1920, **15**, 17, 38, 53; J. S. C. I. 1920, **39**, 314-A, 429-A.

[2] It is best to prepare the sodium stannite solution extemporaneously each time as required, and this may be done by adding a solution of sodium hydroxide to stannous chloride, until the precipitate first formed just dissolves.

Mineral Constituents. A known quantity (about 5 gm.) of the dried guncotton is mixed with an approximately equal quantity of pure paraffin wax[2] in a platinum, quartz or porcelain dish. To facilitate mixing, the dish with its contents are warmed in a steam oven until the wax is melted. The mixture is then ignited. In order that the incineration of the guncotton may take place at a low temperature, it is suggested to ignite the mixture with a glowing platinum wire. The weight of "ash" may be directly determined from the residue on ignition, or the ash may be taken up with ammonium carbonate and heated to 200° until constant in weight. The ash may on the other hand be sulfated and the "ash" determination recorded as sulfate.[1] The absence of ash in the wax is confirmed by carrying out a "blank" with the paraffin alone. "Ash" content may also be determined thus: A weighed quantity of the nitrocellulose is thoroughly moistened with an aqueous solution of ammonium sulfite. It is then ashed in the usual way and the ash sulfated.

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[1] The method of Lunge (J. A. C. S. 1901, **23**, 538) is satisfactory in more highly nitrated products, but is not applicable to the lower nitrates, which Lunge attributes to the fact that as these esters are prepared with less concentrated acid, they invariably contain oxycellulose. The reagent employed is an alcoholic solution of sodium ethylate, C_2H_5ONa, although sodium methylate or amylate would have the same effect and is made by dissolving 2 or 3 gm. metallic sodium in 100 cc. 95% ethyl alcohol, the solution being filtered and mixed with 100 cc. acetone. This reagent has no effect on unaltered cellulose, even after several hours' contact, while the cellulose nitrates are almost instantly decomposed with formation of a reddish brown substance soluble in water (evidently the sodium salt of an organic acid, perhaps oxypyruvic acid, W. Will, Ber. 1891, **24**, 400). The operation is carried out as follows:

150 cc. of the 200 cc. prepared above is placed in a capsule or Erlenmeyer flask along with 5 gm. of guncotton. The mixture is heated to 40° or 50° on a water bath, and now and then shaken up during twenty or thirty minutes; or else it is allowed to stand at the ordinary temperature for a few hours. It is then allowed to settle. The brown-red solution is decanted from the undissolved portion; the latter is first washed with alcohol by decantation, and subsequently with water, whereby the brown substance is dissolved. The residue, consisting of cellulose, is filtered and washed with hot water, last of all with addition of a little hydrochloric acid. For ordinary work, it may be at once dried and weighed; for very exact estimations the water is removed by washing with alcohol, the residue is once more treated with 50 cc. of the reagent left over from the first treatment by keeping at 40° or 50° for fifteen minutes, and the operation is finished as above. The cellulose thus obtained does not yield a trace of gas in the nitrometer and gives only an extremely faint blue reaction with diphenylamine. It showed a very faint yellow color, produced by about 0.1 mgm. of the brown substance which can be removed by treating with a solution of 0.1 mgm. chloride of lime in 5 cc. very dilute hydrochloric acid; but this last treatment is really unnecessary, as the 0.1 mgm. does not appreciably affect the estimation. The results agree to 0.1% or 0.2%, if the weight of unchanged cellulose amounts to about 0.2 gm., which can be attained by employing a convenient weight of the cellulose nitrate.

[2] F. Hess, Zts. anal. Chem. 1880, **19**, 504; abst. Jahr. Chem. 1880, **33**, 1210, 1309; Chem. News, 1881, **44**, 47; Proc. U. S. Naval Inst. 1881, **7**, 198; Wag. Jahr. 1880, **26**, 374; Chem. Ind. 1880, **3**, 256; Chem. Tech. Rep. 1880, **19**, I, 339.

The nitrocellulose before igniting may also be decomposed by nitric acid. One gram of the dried sample contained in a covered crucible is heated with 10–20 drops of concentrated acid on a steam bath, until the fibrous structure has been broken down and the material takes on a gummy appearance. The crucible is then heated by a Bunsen burner, gently at first to avoid loss of ash by a too rapid discharge of gas out of the crucible, and finally at a red heat. The gain in weight, when burned to constancy, is considered as the ash. A similar method of decomposition (with nitric acid) may be employed in the determination of ash of gelatinized nitrocellulose.

As the amount of ash in guncotton is generally very small, particular metals may be present only in traces. These may often be detected by spectrum analysis or by specific tests. For the detailed examination of the mineral consituents the following method of procedure is recommended by H. Schjerning.[2] 5 grams of the material are placed in a large platinum dish and thoroughly moistened with a mixture of alcohol and ether in which paraffin has been dissolved to saturation, filtered, and mixed with one-fourth of its volume of water. A few pieces of solid paraffin are also added and the mixture then ignited, taking the usual precautions. The residue is taken up with hydrochloric acid (heated to 90°). The oxides of iron, aluminium and magnesium are dissolved while the insoluble portion is usually silica. The

[1] J. C. S. 1868, **20**, 327.

[2] Zts. anal. Chem. 1892, **31**, 283; abst. J. S. C. I. 1893, **12**, 62; J. C. S. 1892, **62**, 1520; Zts. ang. Chem. 1892, **5**, 467; Chem. Centr. 1892, **63**, II, 425; Jahr. Chem. 1892, **45**, 2531; Chem. Ztg. Rep. 1892, **16**, 243; Wag. Jahr. 1892, **38**, 389; Ber. 1892, **25**, 873; Tech. Chem. Jahr. 1892–1893, **15**, 180; Meyer Jahr. Chem. 1892, **2**, 365. Proc. Amer. Pharm. Assoc. **41**, 441.

detailed analysis of the hydrochloric acid extract is carried out by the ordinary methods.

The total unsulfate ash (B%) obtained by H. Schjerning's method may also be treated thus: Heat the ash with a known amount of $N/10$ hydrochloric acid to exactly 90°. Cool, and add a little ammonium chloride and a few drops of litmus solution and then render decidedly alkaline with $N/10$ caustic soda solution. Filter off and weigh impurities (C%) consisting of Fe_2O_3, Al_2O_3 and SiO_2, and titrate back with $N/10$ acid represented by A, and the ccs. of the $N/10$ acid neutralized by the losses in 10 grams of the nitrocotton.

$$MgO = [0.0028A - (B - C)] \times 2.5$$
$$CaO = [(B - C) - 0.002A] \times 3.5$$

In the A. Schrimpff method for the estimation of ash,[1] 5 gm. is saturated with 25 cc. of pure nitric acid (sp. gr. 1.4) in a platinum dish and evaporated to dryness on a water bath. The residue is heated on an asbestos plate, and finally over the naked flame. After cooling it is treated with a little water, again evaporated, and again ignited.

Acidity. The acidity of nitrocottons, according to the U. S. Ordnance methods of testing, may be determined by either of the following procedures: A known quantity (1 gram) of the material is soaked in a glass-stoppered bottle with 25 cc. neutral water for two hours with occasional agitation. The clear supernatant liquid is then withdrawn with a pipette and titrated with $N/10$ or $N/100$ alkali, phenolphthalein or azolitmin being used as indicator. A quick and accurate method is to dissolve 1 gm. nitrocotton in 25 cc. neutral acetone and add this liquid in small portions and with much shaking to 100 cc. neutral water. The nitrocotton is precipitated out and after filtration through paper an aliquot portion of the filtrate is titrated with standard alkali as before. Owing to the difficulty of completely removing the acid by water extraction, it is necessary to have the material in a very finely divided condition, and to extract thoroughly with hot water. The water used should be previously tested for the presence of acidity or alkalinity. This method is applicable also for the detection and estimation of acidity in nitrocellulose powders.

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[1] Zts. Schiess. Sprengs. 1920, **15**, 17, 38, 53; abst. J. S. C. I. 1920, **39**, 314-A.

A. Angeli[1] shows the presence of acidity in nitrocellulose powders by the aid of the indicator, dimethylaminoazobenzene. A few ccs. of distilled water containing 3-4 drops of a 0.2% alcoholic solution of the indicator is poured on about 0.5 gram of the powder. It is claimed that powders of good quality turn lemon-yellow, whereas, if acidity is present, an intense red is produced, the supernatant liquid remaining entirely colorless.

According to A. Angeli and G. Errani,[2] microscopical examination of very thin sections of the powders treated with this indicator shows that in some cases the acidity is distributed throughout the mass of the explosive, whereas in others it is localized in isolated regions often with sharply marked outlines. With certain altered nitrocellulose powders, the intact strips were not colored on immersion in the reagent, but the latter soon assumed a more or less intense pink color; if, however, the strips were broken or scraped, the fresh surfaces thus made were immediately colored scarlet by the indicator. The acids occurring at these surfaces were not completely removed by prolonged washing with boiling water, and were almost insoluble in ether and only partially soluble in alcohol. Towards litmus these strips showed an acid reaction, even at their surface. Colored plates are given showing the different effects obtained.

Alkalinity. Some manufacturers leave traces of sodium carbonate in nitrocotton intended for artificial leather and photographic films in order to neutralize any traces of acid which might subsequently develop. Five gm. of the air-dried sample are finely divided and digested with 25 cc. $N/2$ HCl for one-half hour, the mass diluted to 250 cc. and portions of 25 or 50 cc. each titrated against standard alkali, using azolitmin or methyl orange as indicator.

In the British specification for "guncotton for cordite manufacture" 0.2% to 0.3% of alkali estimated as calcium carbonate is required.

To prepare highly sensitive azolitmin from ordinary litmus,

[1] Atti. R. Accad. Lincei, 1918, **27**, I, 164, abst. J. S. C. I. 1918, **37**, 608-A; C. A. 1919, **13**, 262; Gazz. chim. ital. 1918, **48**, II, 18; Chem. Zentr. 1919, **90**, II, 702. See also Atti. R. Accad. Lincei, 1919, **28**, I, 20; abst. J. C. S. 1919, **116**, i, 196.

[2] Gazz. chim. ital. 1920, **50**, i, 139; abst J. S C. I. 1920, **39**, 479-A.

the following procedure is recommended by J. Meyer:[1] Litmus is mixed with a small quantity of concentrated sulfuric acid. The mixture is dried, pulverized and then extracted with absolute alcohol. The azolitmin is precipitated from the alcoholic extract by the addition of water. The author (Worden)[2] pours glacial acetic acid over litmus and extracts the mass with acetone.

To avoid delay in filtering the hydrochloric acid solution extract of the guncotton (with the possible risk of slight change in the acidity), it is advizable to pipette off a known volume of the liquid for titration. To prevent small particles of guncotton being carried into the pipette a small aluminium cap fitted with filter cloth may be attached to the end of the pipette.

Sulfate (SO_3) in Nitrocotton. It is well known that nitrocottons, even after thoroughly washing with water, usually retain a small quantity of sulfur compounds. The sulfuric acid used in the mixed acids which are employed for nitration acts not only as a dehydrating agent, but also in a smaller degree as a "sulfating" agent. A small quantity of a cellulose sulfate ester is in consequence formed, and this may not be all removed in the purification process. The "SO_4" content of nitrocotton is usually not all derived from the sulfate esters since a small quantity of inorganic sulfate may also be present. Mankowsky[3] found 0.367% sulfuric acid in well washed pyroxylin, of which 0.238% was in the form of sulfates. In pyroxylin less well-washed, this may be as high as 1%. The influence of cellulose sulfo-esters on the stability of nitrocottons is considered in detail in the stability topic. Here we need only consider the method of estimating the "SO_3" content of nitrocotton.

The following method may be employed for the sulfate estimation: 5 grams of dry nitrocotton are digested with 50 cc. of redistilled nitric acid, a crystal of potassium chlorate is added and the whole evaporated nearly to dryness. 5 cc. of concentrated hydrochloric acid and one gram of potassium chlorate are added and the solution evaporated to dryness. This last step (of adding acid, chlorate and evaporation) is repeated. Next the residue is boiled with distilled water, filtered and washed. Barium chloride is added to the filtrate, which is then boiled, filtered and the precipitate washed; the filter paper and contents are then ashed in a weighed silica basin and sulfated in the ordinary way. A blank experiment must be carried out on all reagents. In C. Piest's method[1] 20 grams of nitrocotton are heated with 70 cc. of nitric acid (sp. gr. 1.4) and 1 gram of potassium nitrate. The mixture is evaporated to dryness on the steam bath; the residue is then incinerated carefully and the sulfate in the new residue estimated by extracting with dilute hydrochloric acid and precipitating with barium chloride.

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[1] D. R. P. 262838, 1912; abst. C. A. 1914, **8**, 790; Chem. Zentr. 1913, **84**, II, 634; Chem. Ztg. Rep. 1913, **37**, 681; Wag. Jahr. 1913, **59**, II, 254; Zts. ang. Chem. 1913, **26**, 526; Friedlander, **11**, 735.

[2] The so-called "chemically pure" litmus is used as the starting point, being first dissolved in hot water to a viscous mass. Glacial acetic acid is then added until effervescence ceases, the water-soluble carbonates being thereby converted into the corresponding acetates, soluble in acetone. The deliquescent mass is then evaporated to dryness, powdered, and introduced into a Soxhlet extractor, where it is extracted with acetone as long as the percolate comes through fluorescent. The acetone extracts from 65%–75% of the original purified litmus taken. The material is then removed from the Soxhlet, ground to 100 mesh, and again acetone-extracted. By this treatment the inorganic salts, oil, and erythrolitmin are completely removed. The ash of azolitmin prepared in this manner seldom exceeds 0.2%.

[3] Bull. Soc. Chim. 1885, **43**, 124; abst. Jahr. Chem. 1885, **38**, 2197.

In determination of the sulfur combined as sulfuric esters in nitrocellulose, C. Kullgren[2] is unable to obtain reliable results by decomposition with alkali[3] or with aqua regia.[4] On a sample containing sulfates equivalent to approximately 28 mgm. barium sulfate per gram, the first method gives results varying from 9 to 15 mgm., the second method 11 to 20 mgm. barium sulfate, showing that the organic sulfate is not readily decomposed by these methods. Oxidation with sodium peroxide is also unsatisfactory, results vary from 6.9 to 24.3 mgm. barium sulfate per gram. The following method is found to give good results: 0.7–0.8 gm. nitrocellulose is decomposed by heating for $^1/_2$ hour on a water bath with 10 cc. hydrochloric acid in a small beaker; the denitrated material is then evaporated to dryness in a porcelain boat, and heated in a combustion tube in a current of oxygen. The sulfur dioxide evolved is absorbed in caustic soda.[1] The sulfite is oxidized to sulfate and precipitated as barium sulfate. The results obtained varied from 26-29 mgm. barium sulfate per gram. The nitrocellulose used for the experiment had received only $^1/_4$ the usual boiling in purification. A sample taken after boiling was completed contained 14.4 mgm. barium sulfate per gram of nitrocellulose.

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[1] Zts. ang. Chem. 1913, **26**, 661; abst. C. A. 1914, **8**, 573; J. S. C. I. 1913, **32**, 1087; Chem. Zentr. 1913, **84**, II, 2184; Meyer Jahr. 1913, **23**, 363; Wag. Jahr. 1913, **59**, I, 457. Cf. C. A. 1912, **6**, 1366 Analyst, 1914, **39**, 45.

[2] Zts. Schiess. Spreng. 1912, **7**, 89; abst. Wag. Jahr. 1912, **58**, I, 444; J. C. S. 1912, **102**, ii, 682; C. A. 1912, **6**, 1366; J. S. C. I. 1912, **31**, 303; Chem. Zentr. 1912, **83**, I, 1399; Chem. Ztg. Rep. 1912, **36**, 293.

[3] C. Hake and R. Lewis. J. S. C. I. 1905, **24**, 374, 919; abst. Jahr. Chem. 1905–1908, II, 974; Chem. Centr. 1905, **76**, I, 1702; J. C. S. 1905, **88**, i, 512; Chem. Centr. 1905, **76**, I, 1702; Meyer Jahr. Chem. 1905, **15**, 357; Zts. ang. Chem. 1905, **18**, 1988.

[4] C. Cross, E. Bevan and J. Briggs, Ber. 1905, **38**, 1859, 3531; abst. J. S. C. I. 1905, **24**, 685, 1251; Jahr. Chem. 1905–1908, II, 986; Bull. Soc. Chim. 1906, **36**, 638, 639; J. C. S. 1905, **88**, 512; Chem. Centr. 1905, **76**, II, 36, 1625; Wag. Jahr. 1905, **51**, II, 399.

E. Caron[2] determines combined sulfuric acid by treating the nitrocellulose with hydrogen dioxide and sodium hydroxide solution, heating for 5 min., cooling, repeating the treatment, and then slightly acidifying the mixture with HCl. After filtration the sulfuric acid in the filtrate is precipitated with barium chloride in the usual manner.

V. Hottenroth[3] also employs concentrated hydrochloric acid and heats for several hours until the solution can be diluted without the formation of a precipitate of hydrocellulose.

Mercuric Chloride in Nitrocellulose. The presence of a small quantity of mercuric chloride in guncotton, gelignite, blasting gelatin, etc., interferes with the heat test. As small a quantity as 1 part of mercuric chloride in 100,000 may increase the heat test of a nitrocellulose from 10 minutes to 30-50 minutes or even higher. The presence of mercuric chloride does not necessarily mean that the stability of the nitrocellulose is increased. The presence of the salt masks the true heat test and a false idea of the stability of the explosive may be inferred.[4] It is therefore of importance to be able to carry out the heat test under such conditions that the presence of mercuric chloride will not interfere with the test. This can be done by carrying out the test in presence of silver foil or by the use, instead of potassium iodide, of an indicator which is not affected by mercury salts Independent of the heat test it is of importance to be able to ascertain the actual presence of mercury salts in a nitrocellulose and to be able to determine quantitatively the amount actually present. It is claimed that mercuric chloride is added to wet guncotton to prevent the development of bacteria and molds, and undoubtedly it has this property. It is probably added in certain instances with the object of increasing the difficulty of obtaining a true heat test.[1]

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[1] W. Barlow, J. A. C. S. 1904, **26**, 341; J. Landw. 1903, **51**, 289, abst. J. C. S. 1904, **86**, ii, 82; J. S. C. I. 1904, **23**, 562; Rep. Chim. 1904, **4**, 330; Chem. Centr. 1904, **75**, I, 118; Jahr. Chem. 1904, **57**, 817.

[2] Ann. Chim. Analyt. 1919, **1**, 235; abst. J. S. C. I. 1919, **38**, 741-A.

[3] Chem. Ztg. 1914, **38**, 515; abst. C. A 1914, **8**, 2944; J. S. C. I. 1914, **33**, 476; Chem. Zentr. 1914, **85**, I, 1853; Kunst. 1914, **4**, 239; Zts. ang. Chem. 1914, **27**, II, 461.

[4] W. Hargreaves and W. Rowe, J. S. C. I. 1907, **26**, 813; abst. C. A. 1907, **1**, 2636; Bull. Soc. Chim. 1908, **4**, 58; Rep. Chim. 1907, **7**, 449; Chem. Centr. **78**, II, 1192; Chem. Ztg. Rep. 1907, **31**, 570; Jahr. Chem. 1905-1908, I, 3181; Eng. Min. J. 1907, **84**, 443.

Since mercuric chloride has a strong affinity for organic matter and owing to the fact that a trace only is present, its accurate estimation in nitrocellulose is somewhat difficult. J. Moir[2] employed the following methods for its estimation: His first method is in reality a combination of the older methods of Hargreaves and Rowe[3] and that of E. Mann.[4] The moist guncotton, along with a piece of (ignited) silver foil, is placed in a flask immersed in boiling water, and air is aspirated through it, and then through bulbs containing 2% sulfuric acid. After two hours any mercuric chloride which has escaped the silver becomes deposited thereon by using the foil as anode in electrolyzing the dilute sulfuric acid from the bulbs (two hours with about 4 volts required). The foil is dried and the deposit sublimed on to a microscope slide, as in the other methods.

S. Jannopoulos[5] employs a somewhat similar method, except that he replaces the silver by thin copper foil and uses hydrochloric instead of sulfuric acid. 30-40 grams of guncotton are made into a stiff paste with water and pieces of a bright thin copper sheet placed in it; a few cc. of concentrated hydrochloric acid are added to the paste, which is stirred up and allowed to stand for a few days. The copper pieces are washed with very dilute caustic soda solution, then with distilled water, and finally with alcohol and ether. It is then placed in a desiccator to dry. The copper-strips are rolled up and placed in a glass tube which is open at both ends. A microscope glass slide is placed over the upper opening. The tube is placed in an inclined position and heated in a flame just below the copper roll. The minute drops of mercury collecting on the glass slide can be recognized under the microscope as such, or after the action of iodine vapors upon them as mercuric iodide. Under fixed conditions the resulting stain may be compared with a standard set of stains and the test made approximately quantitative.[1]

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[1] Chem. News, 1908, **97**, 133.

[2] J. Chem. Met. Min. Soc. S. Africa, 1907, **8**, No. 7; Chem. News, 1908, **97**, 133; Chem. Zentr. 1908, **79**, I, 1650; Jahr. Chem 1905–1908, II, 980; J. S. C. I. 1908, **27**, 421.

[3] See J. Henderson and P. Jones, Proc. Roy. Soc. Queensland, **21**, 51; abst. C. A. 1909, **3**, 1460.

[4] J. Chem. Met. and Min Soc S. Africa, 1907, **8**, No. 7; abst. J. S. C. I. 1908, **27**, 421.

[5] Zts. Schiess. Sprengs 1910, **5**, 47; abst. J. C. S. 1910, **98**, ii, 549; Chem. Zentr. 1910, **81**, I, 1651; Jahr. Chem. 1910, **63**, 425; C. A. 1910, **4**, 1100. 7th Inter. Cong. Appl. Chem; J. S. C. I. 1910, **29**, 235; Meyer Jahr. Chem. 1910, **20**, 328, Wag. Jahr. 1910, **56**, I, 496; Zts. ang. Chem. 1910, **23**, 1963.

The second method of J. Moir consists in conversion of the mercury salt into a non-volatile compound. The cotton is extracted with hot, very weak potassium iodide solution, and the extract (containing K_2HgI_4) concentrated to a small bulk and electrolyzed. Iodine separates on the platinum basin used as cathode, and the whole of the mercury collects on the gold or silver foil anode after two or three hours, and is worked up as above. The latter method is the quickest and most sensitive the author has as yet tried, and has the advantage of absence of all danger of explosion.

C. Wolff[2] has also described a method of separating traces of mercury by electrolysis from liquids containing much organic matter. He uses a strong platinum wire spiral for the positive electrode and for the negative electrode a thin iron wire which is first coated with copper and finally with silver. After the mercury is deposited the cathode is withdrawn, washed with water, alcohol and ether, and the mercury then volatilized and deposited in the cool portion of a narrow tube. A small quantity of iodine is then introduced and volatilized by gentle heat. On ascending the tube it changes the metallic mercury into the iodide. The method is extremely delicate; 0.00001 gram of mercury dissolved in 100 cc. of water gives a very distinct ring of the iodide. The test may be made quantitative.

J. Berkhout[3] dissolves 2 grams of nitrocellulose or nitrocellulose powder in 20 cc. acetone, and transfers it to a mortar containing finely ignited copper oxide; he mixes to form a granular dry mass, allowing the acetone to evaporate. The mixture is placed in one end of a glass tube (500 x 14 mm.) and more copper oxide added. The empty end of the tube is then heated and drawn out to form bulbs connected by capillaries. A bent delivery tube connects the tube with water in a beaker. The mixture in the tube is heated carefully over burners so that a slow current of bubbles passes through the beaker, the four bulbs being cooled with water. After evolution of gas ceases, the portion of tube beyond the copper oxide is fused off, the mercury condensed in the bulbs is washed out and collected on a watch glass, and the diameter of the globule measured by means of the microscope. From the diameter the weight of mercury is calculated. Larger globules are weighed direct.

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[1] The mercury may also be vaporized and the vapors allowed to impinge on a piece of gold foil, the mercury amalgamating with the gold.

[2] Zts. ang. Chem. 1888, **1**, 294; abst. J. C. S. 1889, **56**, 441; Ber. 1888, **21**, R-454; Chem. Ind 1888, **11**, 525; Jahr. Chem. 1888, **41**, 2558; Wag. Jahr. 1888, **34**, 522.

[3] Zts. Schiess. Spreng. 1912, **7**, 67; abst. C. A. 1912, **6**, 1366; J. C. S.

By the aid of spectrum analysis (as pointed out by Dr. Dupré[1]) the presence of traces of mercury salts in nitrocellulose may be detected. G. Patterson[2] has described simplified methods of preparation for the spectroscopic testing of nitrocellulose for mercury. Two gm. samples are dissolved in organic solvents and electrolyzed directly in the solvent, or, when only partly soluble, extracted by such solvents, and the residue treated with nitric acid to destroy all organic material, the residue being extracted with water and electrolyzed. Metallic mercury is detected by the modified or second method. The method is also applicable for separation for quantitative determinations. The method is accurate to 0.000001 gm. of mercury, but fails with less than 0.0000001 gm. of mercury.

J. Florin[3] has also described in detail a spectroscopic method for the analysis of nitrocellulose. The method is applicable in addition to the identification of other methods.

Determination of Fineness. To determine the "fineness"

1912, **102**, ii, 689; Chem. Zentr. 1912, **83**, I, 1251; Wag. Jahr. 1912, **58**, I, 444. In this connection see P. Raaschou, Zts. anal. Chem. 1910, **49**, 172; abst. Chem. Zentr. 1910, **81**, I, 1643.

[1] J. S. C. I. 1907, **26**, 813.

[2] 7th Inter. Cong. Appl. Chem.; abst. Zts. Schiess. Spreng. 1910, **5**, 14; C. A. 1909, **3**, 2226; J. S. C. I. 1909, **28**, 747; J. C. S. 1911, **100**, ii, 442; Zts. ang. Chem. 1909, **22**, 1119. See also C. A. 1907, **1**, 2411, 2636; 1908, **2**, 708, 3146; 1909, **3**, 836, 1460; 1910, **4**, 961.

[3] Zts. Schiess. Spreng. 1911, **6**, 21, 63; abst. Wag. Jahr. 1911, **57**, I, 477; C. A. 1911, **5**, 2177; J. C. S. 1911, **100**, ii, 1033; Chem. Zentr. 1911, **82**, I, 1453. Ann. Mines Belg. 1910.

of various nitrocottons the following method may be employed: 10 grams of dry nitrocellulose are weighed out and transferred to a 250 cc. stoppered cylinder and 100 cc. of $N/10$ hydrochloric acid and 100 cc. of distilled water added. The cylinder is then shaken up for two or three minutes until no particles of nitrocotton show a tendency to float on the surface of the liquid, and finally allowed to stand, the time being noted. At the end of half an hour the volume occupied by the solid in the cylinder is read off; this gives the fineness. Corrections have to be made for different shaped cylinders, and for this reason it is customary to use the same kind during a series of comparative tests. After the cylinder has stood a further half hour, 100 cc. of the clear liquid are pipetted off and transferred to a conical flask where it is titrated against $N/10$ caustic soda solution, methyl orange being used as indicator. If x cc. is the amount of $N/10$ NaOH required then the percentage of alkalinity calculated as $CaCO_3$ is:

$$\frac{50 - x}{10}$$

Another test sometimes carried out consists in thoroughly wetting a definite weight of nitrocotton with a large excess of water in a stoppered measuring cylinder. The cylinder and contents are allowed to settle and the volume of the nitrocotton read off. When the test is carried out under standard conditions, the settling test gives figures for comparison of fineness of various products.

Determination of Density. There are several methods for determining the specific gravity of dry and wet compressed guncotton, and in the latter case, knowing the moisture content, the density may be obtained. Weighing wet blocks in water and then in air is a ready approximate method, or planing wet guncotton blocks into cubical form, measuring in order to obtain the cubical contents and then weighing is also rapid and fairly accurate.

The method of determining the density as described by Bode, making use of the Bode densimeter, is perhaps the most accurate, considering the time involved in making the determination, and is found by determining the space which a quantity of the nitrocellulose of known weight occupies; or inversely, by determining the weight of a given quantity of material filling a known space.

In practice, however the latter method is nearly always used.

The apparatus consists of a base plate with standard, and a movable bracket carrying a glass vessel into which the framework of a scale dips. The upper rim of the glass vessel is ground off, and is made of strong glass in order to withstand the pressure of mercury on it. The scale is of steel, the three arms being connected on the top by a horizontal triangular frame, the central boss of which is perforated.

Three steel pins are firmly screwed on to this boss. A disc with three perforations through which the steel pins pass, carries a vertical graduated scale, which passes through the whole of the boss, the reading being taken on the upper edge of the latter. The disc is made sufficiently heavy to just float on the mercury. The apparatus is set up perfectly horizontal on a table by means of adjusting screws, and the glass filled with chemically pure mercury free from dust. The specific gravity of the mercury is either determined in the usual manner, or by a steel capsule of 217 gm. weight, the sp. gr. of which at 13.75° is 7.6552. After the room temperature has been noted, the steel capsule is floated on the mercury, and the weighed scale put on to it.

Weights are then placed on the scale until the capsule is pressed so far down that the disc just touches the surface of the mercury. If the weight of the capsule be S, and its sp. gr. p, the weight of the scale W, the weights placed on it G, and the weight of the mercury displaced Q, then

$$Q = G + W + S$$

The volume of the steel capsule is $V = \dfrac{S}{p}$

and hence the sp. gr. of the mercury is $P = \dfrac{Q}{V} = \dfrac{(G + W + S)p}{S}$

The upper tap is next closed and the lower one opened, the cylinder is filled with mercury and again weighed. The difference between the two weighings of the cylinder, i. e., with and without the nitrocellulose, enables the density of the latter to be calculated as follows:

Let P equal the weight of nitrocellulose used. T is the weight of the steel cylinder with the mercury.

Ti = T + the material.
t° = temperature of the Hg.
S = density of material.

$$\text{Then, } S = \frac{P\,13.59(1 - 0.00018\,t^\circ)}{T - Ti + P}$$

The Determination of Nitrogen. Many methods have been suggested for the determination of nitrogen in nitric esters. The most generally employed process is that worked out by Lunge. The principle of this method depends on the following reaction, which was first investigated by W. Crum.[1]

$$2KNO_3 + 4H_2SO_4 + 6Hg = 3Hg_2SO_4 + K_2SO_4 + 4H_2O + 2NO$$

a similar type of reaction occurs with cellulose nitrate and all the nitrogen is obtained in the form of nitric oxide.

The determination of nitrogen by the Lunge nitrometer will be first considered.

The influence of slight modifications in the method of carrying out the nitrometer test have been extensively studied. In the reaction between mercury, concentrated sulfuric acid and cellulose nitrate in the nitrometer a small amount of sulfur dioxide is formed.[2] The nitric oxide usually contains traces of carbon dioxide and carbon monoxide formed in the decomposition of the cellulose group. Traces of nitrous oxide and nitrogen may also be present on account of a slight reduction of the nitric oxide.[3] The nitrogen figure obtained by the nitrometer method is usually slightly lower (about 0.2%) than that obtained in the Schloesing's method.[4,5] The investigations of various workers with regard to the importance of these and other factors on the analytical value of the nitrometer determinations will be briefly indicated.[1]

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[1] Ann. 1847, **62**, 233; J. prakt. Chem. 1847, **41**, 201; Phil. Mag. 1847, (3), **30**, 426; J. Pharm. 1847, (3), **12**, 296; Jahr. Chem. 1847–1848, **1**, 1130; Glasgow Phil. Soc. Proc. 1844–1848, **2**, 163; Ann. 1847, **62**, 233.

[2] C. Baskerville and F. Miller, J. A. C. S. 1898, **20**, 515; abst. J. S. C. I. 1898, **17**, 795. J. C. S. 1898, **74**, ii, 22; Jahr. Chem. 1898, **51**, 404. Reply to T. Pitman, J. A. C. S. 1898, **20**, 100; abst. Chem. Centr. 1898, **69**, I, 709. See also C. Baskerville, J. A. C. S. 1895, **17**, 904; Chem. Centr. 1897, **68**, I, 10; J. C. S. 1896, **72**, ii, 474. L. Andrews, J. C. S. 1897, **73**, ii, 22; J. A. C. S. 1896, **18**, 251; Chem. Centr. 1896, **67**, I, 885. S. Pickering, J. C. S. 1878, **33**, 112.

[3] M. Marqueyrol and D. Florentin, Bull. Soc. Chim. 1911, **9**, 231; abst. J. S. C. I. 1911, **30**, 509; C. A. 1911, **5**, 2050; Wag. Jahr. 1911, **57**, I, 476; J. C. S. 1911, **100**, ii, 437; Chem. Zentr. 1911, **82**, I, 1442; Zts. ang. Chem. 1911, **26**, 1380; Chem. Ztg. Rep. 1911, **35**, 301.

[4] M. Koehler and M. Marqueyrol, Ann. chim. anal. 1913, **18**, 91; abst. C. A. 1913, **7**, 2116. J. C. S. 1913, **104**, ii, 241; Bull. Soc. Chim. 1913,

According to E. Berl and A. Jurrissen[2] in the ordinary nitrometer method of determining nitrogen the difficulty in obtaining consistent results is due mainly to the irregular action of the concentrated sulfuric acid in which many gelatinous nitrates are not readily soluble. The acid acting as an oxidizing or dehydrating agent sometimes gives rise to gaseous products other than nitric acid, thus leading to high results. It is also claimed that oxime formation may sometimes occur. This prevents some of the nitrogen being set free and leads on the other hand, to low results.

While a small amount of carbon dioxide and carbon monoxide may be formed in the decomposition of guncotton, greater quantities of these gases will be produced in the analyses of some gelatinized powders. This is due to the increased difficulty in dissolving these materials and the consequently greater action of the acids on the nitrocellulose. In addition such substances as are added either as stabilizers or to reduce muzzle flash may react with the nitrosyl sulfuric acid and so increase the possibility of oxime formation.[3] C. Joyce and H. LaTourette[4] correct, when necessary, for the solubility of nitric oxide in sulfuric acid of 95% concentration. This solubility decreases when the temperature rises above 28°. They also correct for other gases produced by the breaking down of the cellulose molecule in the decomposition

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13, 48, 69; Chem. Zentr. 1913, **84**, I, 1725; Zts. anal. Chem. 1913, **52**, 763; Zts. ang. Chem. 1913, **26**, II, 355. See also C. A. 1911, **5**, 2050; 1913, **7**, 1609.

[5] P. Nicolardot and G. Chertier, Compt. rend. 1910, **151**, 719; abst. Jahr. Chem. 1910, **63**, 423; C. A. 1911, **5**, 1588; J. C. S. 1910, **98**, i, 818; J. S. C. I. 1910, **29**, 1299; Bull. Soc. Chim. 1911, **9**, 856; Chem. Zentr. 1910, **81**, II, 1888; Chem. Ztg. 1910, **34**, 1213; Meyer Jahr. Chem. 1910, **20**, 328.

[1] J Newfield and J. Marx, J. A. C. S. 1906, **28**, 877; abst. J. C. S. 1906, **90**, ii, 628; Chem. Centr. 1906, **77**, II, 816.

[2] Zts. ang. Chem. 1910, **23**, 241; abst. J. S. C. I. 1910, **29**, 374; C. A. 1910, **4**, 1140; J. C. S. 1910, **98**, ii, 240; Chem. Zentr. 1910, **81**, I, 1637; Jahr. Chem. 1910, **63**, I, 594; Meyer Jahr. Chem. 1910, **20**, 328; Zts. ang. Chem. 1910, **23**, 241.

[3] O. Poppenberg and E. Stephen, Zts. Schiess. Spreng. 1909, **4**, 350; abst. J. S. C. I. 1909, **28**, 1064; C. A. 1910, **4**, 1674; J. C. S. 1910, **98**, ii, 451; Chem. Zentr. 1909, **81**, II, 1591; Jahr. Chem. 1909, **62**, II, 48; Wag. Jahr. 1909, **55**, I, 447.

[4] J. Ind. Eng. Chem. 1913, **5**, 1017; abst. C. A. 1914, **8**, 473; Chem. Zentr. 1914, **85**, I, 426; Zts. ang. Chem. 1914, **27**, II, 674.

of the nitrocellulose. The ordinary nitrometer method is not applicable to the analysis of celluloid or substances containing aromatic ring compounds. E. Beckett[1] examined the gases formed in the Lunge nitrometer during the decomposition of guncotton. The determination of nitrogen was carried out by two methods. In the first method (a) a quantity of guncotton was placed in the cup of the nitrometer with successive quantities of 5, 2.5, 2.5 and 5 cc. of sulfuric acid (conc. 96.5). In the second method (b) a similar procedure was adopted except that 1 cc. of water was added before shaking the nitrometer. In method (a) 111–115 cc. of gas were obtained. This gas (mainly nitric oxide) contained 0.4 cc. of a mixture of carbon dioxide and sulfur dioxide, as well as 0.6 cc. of nitrogen. The residual sulfuric acid contains nitrogen equivalent to 0.75 cc. of nitric oxide. The 15 cc. of 96.5% of sulfuric acid used, contained 0.4 cc. of nitrogen gas, of which 0.35 cc. was evolved in the nitrogen determination of the guncotton. Part of the nitrogen in the gas was probably produced by partial reduction of the nitric oxide. The errors produced by these impurities balance one another, so that the gas evolved is supposed to be pure nitric oxide and to contain all and only the nitrogen in the guncotton, correct results are obtained.[2] In method (b) slightly higher results are obtained. The increase in the volume of gas is caused by the presence of a larger quantity of impurities (carbon dioxide, carbon monoxide and sulfur dioxide) in the nitric oxide. The greater quantity of gas was caused solely by the heat evolved on adding the water and was not due to the use of more dilute acid. According to M. Marquevrol and D. Florentin, by employing acid of 94%–94.5% strength, very accurate results are obtained with Lunge's nitrometer as modified by F. Horn[3] without any correction. To obtain consistent results with the nitrometer, A. Herve[4] emphasizes the necessity of verifying that the reaction with the mercury is complete. It is necessary after the volume has been read off to again shake the nitrometer. Two vigorous shakings in all are usually sufficient. If readings still are not constant it is necessary to shake until such is the case. When the volume is constant, very little further variation in the gas volume is noticed if a new reading is taken even after a long interval (2 days). One cause of the divergent results obtained when the test is carried out under different conditions is due to the solubility of the nitric oxide in concentrated sulfuric acid. The solubility is 0.035 cc. per cc. of acid in the case of 94% sulfuric acid. However, in acid of 85% concentration, the gas is insoluble and it is recommended to arrange the test so that the acid in the tube after the nitrocellulose is dissolved (in 96% acid) has a final concentration of 85%.

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[1] J. S. C. I. 1914, **33**, 628; abst. C. A. 1914, **8**, 3120; Chem. Zentr. 1914, **85**, II, 803; 1915, **86**, I, 98; Zts. Schiess. Spreng. 1914, **9**, 394; J. C. S. 1914, **106**, ii, 673; Zts. ang. Chem. 1914, **27**, II, 654.

[2] A. Koehler, M. Marqueyrol and P. Jovinet, Ann. chim. anal. 1913, **18**, 45; abst. C. A. 1913, **7**, 1609; J. S. C. I. 1913, **32**, 253; J. C. S. 1913, **104**, ii, 334; Chem. Zentr. 1913, **84**, I, 1232.

[3] Zts. ang. Chem. 1892, **5**, 200, 358; abst. J. S. C. I. 1893, **12**, 185; Chem. Centr. 1892, **63**, I, 962; Chem. Ind. 1892, **15**, 435; Jahr. Chem. 1892, **45**, 2639; Meyer Jahr. Chem. 1892, **2**, 365; Wag. Jahr. 1892, **38**, 387; Chem. Ztg. 1893, **17**, 1004; Tech. Chem. Jahr. 1891–1892, **14**, 150, 151; Dingl. Poly. 1893, **287**, 93; Arms and Explo. 1892, **1**, 155.

[4] Mon. Sci. 1918, **62**, 241; abst. J. S. C. I. 1919, **38**, 46-A; C. A. 1919,

The pressure exerted on the gas in the nitrometer, according to V. Planchon,[1] causes secondary reaction to occur between the oxide of nitrogen and the sulfuric acid, with the result that erroneous readings are obtained. To avoid these errors the reaction between the mercury, sulfuric acid and guncotton is carried out in a vacuum in a flask attached to a manometer and volumes as great as 50 cc. of sulfuric acid may be employed.

E. Berl and H. Jurrissen also carry out the reaction between the mercury, sulfuric acid and guncotton in a separate vessel (decomposition flask) and measure the gas in a nitrometer. The strong flask (250–300 cc.) employed is fitted with a hollow-ground glass stopper expanding to a pear-shaped top through which the stem of a dropping funnel enters and from which a delivery tube, provided with a three-way cock, leads to a vacuum pump, or an eudiometer, or a carbon dioxide generator. Nitrates, nitrites and nitro-substitution compounds are analyzed by treatment with sulfuric acid and mercury in an atmosphere of carbon dioxide or the first two classes, and by oxidation with sulfuric acid and chromium oxide in vacuo and subsequent treatment with mercury for nitro substances. Using sulfuric acid of a concentration of above 80%

13, 516; Ann. Rep. Soc. Chem. Ind. 1919, **4**, 543; Chem. Zentr. 1919, **90**, II, 622.

[1] Ann. chim. anal. 1915, **20**, 189; abst. C. A. 1916, **10**, 969; J. C. S. 1915, **108**, ii, 793; J. S. C. I. 1915, **34**, 1031; Chem. Zentr. 1916, **87**, I, 726; Zts. Schiess. Spreng. 1916, **11**, 22.

the nitrogen is set free as nitric oxide and may be collected for measurement in an eudiometer filled with 20%–30% potassium hydrate solution or saturated sodium sulfate solution or mercury, but a few cc. of potassium hydrate solution must be used with sodium sulfate or mercury in order to absorb carbon dioxide. The method is accurate not only in the case of cellulose nitrate, but also with compounds of the type of potassium nitrate, and (after oxidation) with such compounds as the nitro-derivatives of toluene, phenol, naphthalene, aniline, etc. The method is also suitable for the determination of nitrogen in gelatinized nitrocellulose, dynamite and nitroglycerol.[1] Amide and imide nitrogen are not affected in this process, making it possible to determine the nitrogen in cellulose nitrate even when such compounds as *p*-nitrosodimethylaniline or such stabilizers as urea or diphenylamine are present. The preliminary oxidation avoids the errors which the presence of bodies like vaseline, camphor, etc., introduce into the ordinary determinations.

A gravimetric method may also be employed for the determination of nitrogen in nitric esters. An apparatus called a nitro-gravimeter (see Fig. 287) has been suggested by B. Oddo.[2] A weighed quantity of the substance for analysis is placed in flask, *A*, with a little sulfuric acid as solvent and the tube *D* containing mercury in excess of the weight of sulfuric acid used is introduced. The mercury employed should be purified before use, with potassium cyanide solution (2%).[3] The stopper with the tubes *B* and *C* fitted is then inserted. Tube, *C*, contains a small quantity of sulfuric acid. Dry carbon dioxide is aspirated through the apparatus until all acid is expelled (taking about 40–45 minutes).

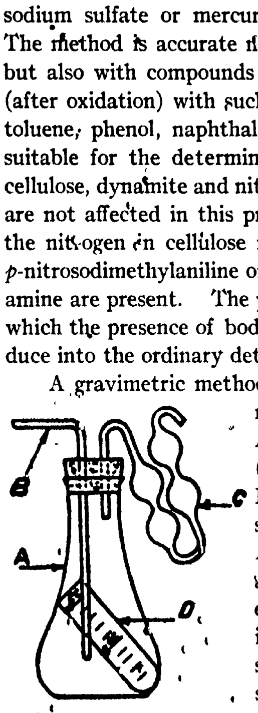

FIG. 287.—ODDO NITRO-GRAVIMETER

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[1] D. Stanojewitsch, Zts. ang. Chem. 1894, **7**, 676; abst. Chem. Centr. 1895, **66**, I, 132; Jahr. Chem. 1894, **47**, 2665; J. C. S. 1895, **68**, ii, 243; Wag. Jahr. 1894, **40**, 510; J. S. C. I. 1895, **14**, 186, 199.

[2] Gazz. chim. ital. 1917, **47**, II, 145; abst. J. S. C. I. 1917, **36**, 1195; C. A. 1918, **12**, 1124; J. C. S. 1918, **114**, ii, 48.

[3] W. Bettel, Chem. News, 1908, **97**, 158; abst. C. A. 1908, **2**, 1645; J. C. S. 1908, **94**, ii, 382; J. S. C. I. 1908, **27**, 407; Bull. Soc. Chim. 1909, **6**, 399; Chem. Zentr. 1908, **79**, I, 1672.

The tubes *B* and *C* are then closed and the apparatus weighed. The tube *C* is then opened and the contents of *D* allowed to fall into the acid by tipping the flask. The apparatus is shaken with a circular motion and also gently heated until the bubbles of nitric oxide pass regularly through the acid in *C*. The evolution of gas is complete in 3–4 minutes and the flask is connected with the carbon dioxide generator to remove the remaining nitric oxide. The loss in weight gives the amount of nitric oxide. The percentage of nitrogen 0.46684 *G* (100/*W*) where *G* = nitric oxide evolved and *W* = weight of sample taken.

When nitrocellulose is boiled with ferrous chloride in presence of hydrochloric acid all the nitrogen is evolved as nitric oxide. This reaction as originally worked out by P. Champion and H. Pellet[1] is not used now in the original form, but a modification known as the T. Schloesing method[2] as modified by Schultze-Tiemann and R. Schmidt, is employed in many laboratories, especially as a control test.[3]

The apparatus consists of a strong flask (200 cc. capacity)

[1] Compt. rend. 1876, **83**, 707; abst J. C. S. 1877, **31**, 228; Ber. 1877, **10**, 735; Chem. Centr. 1877, **48**, 323, 739; Wag. Jahr. 1876, **22**, 479; 1877, **23**, 385; Chem. Tech. Rep. 1876, **16**, I, 388; Jahr. Chem 1877, **30**, 1159; Jahr. rein Chem. 1877, **5**, 175. See also Mon. Sci. 1876, **18**, 1160. See also Ber. 1876, **9**, 1610; Chem. News, 1876, **34**, 205; Zts. Chem. Grossgew. 1876, **1**, 233.

[2] Ann. Chim. Phys. 1854, (3), **40**, 479; abst. Chem. Centr. 1854, **25**, 509; Jahr. Chem. 1854, **7**, 662; J. prakt Chem. 1854, **62**, 142. For improvements on this method see L. deKoninck, Zts. anal. Chem. 1894, **33**, 200, abst. J. C. S. 1894, **66**, 266. J. Newfield and J Marx, J. A. C. S. 1906, **28**, 877; abst. Chem. Centr. 1906, **77**, II, 816. C. Davidson, Chem. News, 1900, **81**, 97. V. Planchon (Ann. Chim. Analyt. 1915, **20**, 189; abst. J. S. C. I. 1915, **34**, 1031; J. C. S. 1915, **108**, ii, 793; Chem. Zentr. 1916, **87**, I, 726; Zts. Schiess. Spreng. 1916, **11**, 22) for the manonitrometric analysis of nitrocotton, which consists of a flask fitted with a three-way metallic stopper allowing connection with the atmosphere and/or with a barometer tube dipping into mercury and furnished with a movable scale. A rubber ring between the stopper and the flask, compressed by a screw frame in which the flask is clamped, ensures air-tightness. A known weight of nitrocotton (about 2.5 gm.) and fixed volumes of sulfuric acid and mercury are placed in the flask, which is then exhausted by a water-pump. The scale is adjusted so that the mercury in the barometer tube stands at zero, and the flask is shaken violently until the pressure remains stationary. It is then immersed in water and the temperature taken. From the temperature, pressure, weight of guncotton, and the known capacity of the flask and barometer tube, the degree of nitration may be calculated. About 5 gm. is used for the analysis of nitrating acids. Variations in the strength of the sulfuric acid employed between 90% and 97% do not sensibly affect the accuracy of the method. Refer to A. Wohl and O. Poppenberg, Ber. 1903, **36**, 676; abst. J. S. C. I. 1903, **22**, 442. A. Wohl, Ber. 1902, **35**, 3485, 3493.

[3] A. Koehler, M. Marqueryrol and H. Loriette, Ann. Chim. anal.

fitted with a two-hole rubber stopper for two tubes. One of the tubes (*a*) passes to the lower end of a water-jacketed measuring tube (containing sodium hydrate solution, sp. gr. 1.25). The second tube (*b*) passes into a test tube (*c*). This latter tube is used for the introduction of liquids into the flask. Each tube has a rubber connection and may be closed by means of a pinch-cock. 0.5–0.65 gram of the dry finely divided nitrocellulose is placed in the flask and 25 cc. of boiling water added. The contents of the flask are boiled in order to free the apparatus from air. The pinch-cocks on the two tubes are then closed and the source of heat removed. 25 cc. of concentrated solution of ferrous chloride and 10–15 cc. of concentrated hydrochloric acid are boiled in the test tube and then introduced by means of the tube (*b*) into the flask, care being taken to prevent the entrance of air. A few cc. of water are next introduced in order to wash in the remainder of the acid. The tube (*b*) is again closed and the contents of the flask heated. When the rubber-tube connections become slightly inflated the pinch-cock in tube (*a*) is opened and the gas collected in the measuring tube. The evolution of gas continues for about 15 minutes. More boiling water is then run into the flask and the contents again boiled. The operation is repeated as long as any extra gas is collected in the measuring tube. The usual method is employed to obtain the volume of the evolved gas at normal temperature and pressure.

The chief sources of error in the modified Schloesing method are caused by the presence of air in both the carbon dioxide and the hydrochloric acid. The nitric oxide also[1] reacts to a small extent with the alkali in the nitrometer forming potassium nitrate, nitrous acid and nitrogen. There is also some difficulty in completely removing carbon dioxide from the nitric oxide. To allow for these errors it is suggested that the experiment should be carried out under carefully standardized conditions. It has already been mentioned that in the determination of nitrogen in guncotton a slightly higher result is obtained in the Schloesing as compared with the nitrometer method. This refers to purified

1914, **19**, 129; abst. C. A. 1914, **8**, 2858; J. C. S. 1914, **106**, ii, 485; Chem. Zentr. 1914, **85**, I, 1974; Zts. ang. Chem. 1914, **27**, II, 661. A reply to H. Pellet, Ann. Chim. anal. 1911, **16**, 294; Chem. Zentr. 1911, **82**, II, 1060; C. A. 1911, **5**, 3663. See also E. Beckett, J. S. C. I. 1914, **33**, 628. A. Dambergis, Oesterr. Chem. Ztg. 1898, **1**, 385; abst. Chem. Centr. 1898, **69**, II, 1296.

guncotton. In the case of unpurified guncotton considerably higher results are obtained by Schloesing method. This is due to the fact that there are unstable nitrous acid esters present in unpurified guncotton. These compounds are decomposed in the cold by concentrated sulfuric acid and hence some nitric oxide is lost before the material enters the nitrometer. Unpurified guncotton may also contain substances which interfere with the reaction of the mercury and prevent the nitrogen being liberated as nitric oxide. This will be, therefore, a second possible source of error.

When nitroglycerol is present in an explosive the above method—using ferric chloride and hydrochloride acid—is not applicable without modification, owing to the volatility of the nitroglycerol. O. Poppenberg and E. Stephan, in determining the nitrogen content of gelatinized powders containing nitroglycerol, make use of a bomb having gas outlets both at the top and bottom. The explosive (1 gram.) is mixed with an equal weight of copper oxide and the mixture placed in a cylindrical iron cup having a stout copper wire projecting from the bottom into the interior. The copper wire serves, when the cup is introduced into the bomb, as the lower terminal for the current, and is connected with the upper insulated terminal by a thin platinum wire 0.1–0.15 mm. diameter. The mixture which surrounds this platinum wire is burned on the passage of the current. Very small density charges may be employed (such as 0.06) without any appreciable formation of oxides of nitrogen or ammonia. The firing takes place in an atmosphere of carbon dioxide and the evolved nitrogen is measured over potassium hydroxide solution. The results agree favorably with those obtained with the Lunge nitrometer method; the method of distillation with sulfuric acid or phosphoric acid and titration of distillate with standard alkali; the stannous sulfate method of A. Longi, and the stannous chloride method of Gay-Lussac.

The method of Dumas may also be employed for the estimation of nitrogen in guncotton. It is necessary to mix the nitrogen-containing substance with a large amount of inert material. In comparative determinations with the nitrometer, Kjeldahl and "nitron" methods, it gives approximately similar results. The method, however, for guncotton is practically obsolete. When nitrocellulose is saponified by boiling with sodium hydrate solution, there are formed alkali nitrates, alkali nitrites and small quantities of ammonia. An oxime-like ketonic or aldehydic compound is also formed.[1] The tendency of nitric groups to split off from the esters and to become reduced to nitrites and ammonia is prevented by the presence of hydrogen peroxide in the reaction mixture.[2] In the presence of the oxidizing agents the whole of the nitrogen is obtained as "nitrate," on acidifying. The nitrate may be estimated by various methods. An estimation involving the use of diphenylenedianilodihydrotriazole (nitron) is simple to carry out and the results agree with the nitrometer figure.[3,4] The determination may be carried out as follows: In an Erlenmeyer flask (150 cc.) is placed 0.2 gram of nitrocellulose, 5 cc. of sodium hydrate solution (30% conc.) and 10 cc. hydrogen peroxide. The mixture is heated on the water bath until the nitrocellulose is dissolved. 40 cc. of water and a further 10 cc. of hydrogen peroxide are added and 40 cc. of dilute sulfuric acid (5% concentration) run in by means of a pipette at the bottom of the flask. The flask is then heated to 80° and 12 cc. of nitron acetate solution added. The flask and contents are then cooled and placed in an ice-chest for a few hours. The precipitate is filtered off and washed with 10 cc. of ice-water in 3–4 portions, and dried to constant weight at 110°. The determination of the nitric acid and incidentally of the nitrogen in the original guncotton is easy to carry out. The results of the nitrogen determination agree closely with the figure given by the nitrometer. The use of nitron as a quantitative reagent has been extended to the analysis of trinitrocresol and its compounds, mixtures of picric acid and dinitrophenol, mannitol and starch nitrates and also to nitroglycerol.[5] The addition-compound of nitron and picric

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1. M. Busch, Zts. ang. Chem. 1906, **19**, 1329; abst. Jahr. Chem. 1905–1908, II, 975; Wag. Jahr. 1906, **52**, I, 498; J. C. S. 1906, **90**, ii, 708; Chem. Centr. 1906, **77**, II, 1020; Meyer Jahr. Chem. 1906, **16**, 325.
2. M. Busch, Ber. 1906, **39**, 1401; abst. Chem. Centr. 1906, **77**, I, 1675; J. C. S. 1906, **90**, ii, 708.
3. M. Busch and S. Schneider, Zts. Schiess. Spreng. 1906, **1**, 232; abst. Chem. Centr. 1906, **77**, II, 1020; J. S. C. I. 1908, **27**, 715.
4. C. Haeussermann, Ber. 1903, **36**, 3956; abst. Chem. Centr. 1904, **75**, I, 160; Jahr. Chem. 1903, **56**, 1017, Wag. Jahr. 1903, **49**, 345; Meyer Jahr. Chem. 1904, **14**, 370; J. S. C. I. 1904, **23**, 36.
5. W. Cope and J. Barab, J. A. C. S. 1917, **39**, 504; abst. C. A. 1917, **11**, 1301; J. C. S. 1917, **112**, ii, 268; J. S. C. I. 1917, **36**, 473; Bull. Soc. Chim. 1917, **22**, 556; Wag. Jahr. 1917, **63**, I, 256.

acid and trinitrocresol are the most insoluble compounds of the trinitrophenols known.

The volumetric determination of the nitric acid in sulfuric acid may be carried out by means of stannous sulfate[1] according to the equation

$$4SnSO_4 + 4H_2SO_4 + 2HNO_3 = 4Sn(SO_4)_2 + 5H_2O + N_2O$$

using diphenylamine as indicator. E. Bronnert[2] has further studied this reaction and has extended the method of A. Longi so that it may be used for the nitrogen estimation in nitrocellulose, potassium nitrate and spent nitrating acids.

Instead of estimating directly the nitric acid formed in the alkali hydrolysis in the presence of hydrogen peroxide, it may be reduced and the resulting ammonia estimated. The reduction is conveniently carried out by the aid of Devarda's alloy. The following procedure is suggested by A. Koehler, M. Marqueyrol and P. Jovinet.[3] It is claimed that the results are concordant and accurate, agreeing well with comparative estimations made by the nitrometer and Kjeldahl methods. Nitrocellulose (0.7 gram) is first moistened with a little alcohol in a 100 cc. flask. 30 cc. hydrogen peroxide, 60 cc. water and 50 cc. potassium hydroxide solution (sp. gr. 1.3) are next added. The mixture is heated on the water bath with frequent shaking until the nitrocellulose dissolves. If a yellow color is produced the nitrocellulose has been heated too strongly or suddenly. The flask with contents is finally heated over a flame until oxygen ceases to be evolved, when it is allowed to cool. 5 cc. of alcohol and 2.5 grams of Devarda's alloy (aluminium 45, copper 50, zinc 5) in a finely divided state, are then added and connected at once to a Wagner distillation tube drawn to a point which dips into the flask containing 25 cc. of 0.33 *N* sulfuric acid and 50 cc. of water. After about 20 minutes the vigorous evolution of hydrogen slackens and the flask is gently warmed to complete reaction. About half the contents of the flask are then distilled. The condenser is kept water cooled. A "back" titration with 0.2 *N* ammonia solution using an alcoholic solution of methyl red as indicator is carried out. A blank test is also made on the reagents.

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[1] A. Longi, Zts. anal. Chem. 1885, **24**, 23; abst. Chem. News, 1885, **51**, 76; J. C. S. 1885, **48**, 595; J. S. C. I. 1885, **4**, 368; Chem. Ind. 1885, **8**, 86; Chem. Tech. Rep. 1884, **28**, II, 182; Jahr. Chem. 1885, **38**, 1910; Wag. Jahr. 1885, **31**, 264; Pharm. Ztg. 1885, 156.

[2] Bull. Soc. Ind. Mulhouse, 1910, **80**, 254; abst. J. S. C. I. 1910, **29**, 1411; C. A. 1911, **5**, 1515; Kunst. 1911, **1**, 453; J. C. S. 1910, **98**, ii, 1116.

[3] Ann. Chim. anal. 1913, **18**, 45; abst. J. S. C. I. 1913, **32**, 263; C. A. 1913, **7**, 1609; J. C. S. 1913, **104**, ii, 334; Chem. Zentr. 1913, **84**, I, 1232.

The Kjeldahl method[1] has been employed for the determination of nitrogen in nitro-explosives by M. Chenel and others.[2] Substances like collodion and guncotton are not estimated in practice by this method, though it is claimed that if the materials are in a very finely divided condition the estimation may be successfully carried out. By the following modified Kjeldahl method the nitrogen in nitro-substituted compounds may be determined within 0.2%. 'About 0.5 gram of the nitrosubstitution compound is accurately weighed and placed in a 500 cc. long-necked Kjeldahl flask. 30 cc. of pure sulfuric acid (96%) containing 2 grams of pure salicylic acid are then added and the nitro-compound dissolved by rotating the flask, or by heating over the steam bath if necessary. After cooling, add 2 grams of zinc dust in small portions at a time, continually rotating the flask to prevent heating much above room temperature. After all of the zinc is added rotate the flask every ten minutes for about one and a half hours and then let stand over night at room temperature. Heat the flask very gently over a small flame until evolution of fumes has ceased (requiring usually 2-3 hours), then bring to boiling and continue boiling for about 2 hours longer. Now add, after cooling, 7.5 grams powdered potassium sulfate (K_2SO_4) and 10 cc. more sulfuric acid, and boil for two hours longer. If the solution is clear and practically colorless the process is complete; if not, add about 1 gram more of the potassium sulfate and boil one-half to one hour longer.' Cool the solution in the flask and add 250 cc. distilled water to dissolve the cake formed; then add 25 cc. potassium sulfide solution (8% strength), 1 gram of granulated zinc and 85 cc. concentrated sodium hydroxide solution, and distil off the ammonia into standard acid solution, completing the determinations as usual in all modification of the method. A blank determination should be made using pure cane sugar as sample instead of the nitro-compound, in order to correct for any nitrogen in the reagents. It is also necessary to check the method with pure picric acid or other pure nitro-substitution compound.[1]

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[1] J. Kjeldahl, Zts. anal. Chem. 1883, **22**, 366; abst. J. C. S. 1884, **46**, 364; Chem. News, 1883, **48**, 101, 118. See also Zts. ges. Brauwesen. 1886, No. 5.

[2] M. Jodlbauer, Chem. Centr. 1886, **57**, 433; abst. Chem. News, 1887. **56**, 91; J. C. S. 1886, **50**, 834; J. S. C. I. 1886, **5**, 510; Chem. Ind. 1886, **9**, 263; Chem. Tech. Rep. 1886, **25**, II, 336; Jahr. Chem. 1886, **39**, 1914. Arms and Expl. 1893, **1**, 87. B. Dyer, J. C. S. 1895, **67**, 811.

According to P. Nicolardot and H. Vouloud,[2] estimation of nitrogen in celluloid and explosives by the nitrometer usually gives too low results. It is found that the camphor present reacts with the nitrocellulose in presence of sulfuric acid, and it is advizable, therefore, to carry out the estimation after precipitating the nitrocellulose from an acetone solution of celluloid by means of benzene, which retains the camphor in solution. Diphenylamine, present as a stabilizer, also causes erroneous results, the nitrogen figure being 0.7% too low.

In a recent comprehensive investigation,[3] E. Beckett has investigated the factors which cause small variations in volume of nitric oxide gas when determining nitrogen in nitrocellulose by means of the nitrometer, and has endeavored to show how more trustworthy results may be obtained by a compensation of errors, due to the fact that several factors are known which influence considerably the course of the reaction.

M. Marqueyrol and D. Florentin[4] had previously pointed out that prolonged shaking of the nitrometer contents caused a diminution of volume by reduction of the nitric oxide gas, and also reabsorption of some of the nitrogen by the sulfuric acid. The cause of the error, however, becomes practically negligible, where the shaking is not unduly prolonged, and the concentration of the sulfuric acid not too high.

Beckett records an experience with guncotton and 96.8% sulfuric acid, where the original volume of gas in the nitrometer was reduced from 109.95 cc. to 109.8 cc. after standing for 26½ hours. The time factor and the concentration of the acid is shown in the following table:

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[1] G. Alberts, Dingl. Poly. 1886, **262**, 227; abst. Wag. Jahr. **32**, 322. . Baucher, Ann. chim. anal. **5**, 373; abst. Chem. Centr. 1900, **71**, II, 1161. E. v. Keussler, Zts. anal. Chem. 1893, **32**, 51; Chem. Ztg. Rep. 1893, **17**, 6; J. C. S. 1893, **64**, ii, 184. H. Pellet, Ann. chim. anal. 1911, **16**, 294; abst. J. C. S. 1911, **100**, ii, 930. G. Lunge, Zts. ang. Chem. 1892, **5**, 261. Chem. News, 1872, **25**, 200.

[2] Chim. et Ind. 1919, **2**, 1317; abst. J. S. C. I. 1920, **39**, 174-A.

[3] J. C. S. 1920, **117**, 220; abst. J. S. C. I. 1920, **39**, 386-A.

[4] Bull. Soc. Chim. 1911, (4), **9**, 234; abst. J. S. C. I. 1911, **30**, 509; C. A. 1911, **5**, 2050; Wag. Jahr. 1911, **57**, I, 476; J. C. S. 1911, **100**, ii, 437; Chem. Zentr. 1911, **82**, I, 1442; Zts. ang. Chem. 1911, **26**, 1380; Chem. Ztg. Rep. 1911, **35**, 301.

DETERMINATION OF NITROGEN IN GUNCOTTON WITH VARIOUS STRENGTHS OF SULFURIC ACID AND THE EFFECT OF ALLOWING THE MIXTURE TO STAND BEFORE BEING SHAKEN.

Sulfuric Acid Per cent.	Interval Between Introducing the Guncotton and Acid into the Nitrometer and Shaken Being:				
	No Time	$^1/_4$ Hour	$^1/_2$ Hour	1 Hour	17–20 Hours
99.87	12.63	......	......	11.76	......
	12.50	......	......	11.82	......
96.80	12.94	......	......	12.74	10.14
	12.945	......	......	12.68	10.28
	12.93	......	......	......	10.71
	12.96	......	......	......	......
94.0	12.975	13.065	......	13.04	11.90
92.5	12.73	13.04	13.035	13.015	12.69
	12.57	......	......	......	......

In a prior communication,[1] the author attacked the problem in a different manner, and found that with guncotton and 96% sulfuric acid, the various errors balance one another, and that the results obtained, therefore, are substantially correct. His method of procedure is as follows:

Dried and sieved nitrocellulose (0.5–0.55 gm.) was placed in a weighing bottle and heated to 96° in a steam bath for one hour. The weighing bottle was then accurately weighed, the nitrocellulose dropped into the cup of the nitrometer, and the empty weighing bottle re-weighed. Five cc. of the sulfuric acid of the specified strength were added to the nitrometer cup, the nitrocellulose stirred in the acid with a glass rod, and admitted to the nitrometer tube. The cup was then washed with successive quantities of 2.5 cc., 2.5 cc. and 5 cc. of the same acid, and these run into the nitrometer. The entire operation of washing the nitrocellulose into the nitrometer with the 15 cc. acid occupied 5 minutes. After the introduction of acid and nitrocellulose, the nitrometer was allowed to stand for a specified time, and then vigorously shaken for $1^1/_2$ minutes. It was allowed to stand for 10 minutes, again vigorously shaken for one minute, and the gas transferred to the measuring vessel. The results obtained are shown in the following table.

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[1] J. S. C. I. 1914, **33**, 628; abst. C. A. 1914, **8**, 3120; Chem. Zentr. 1914, **85**, 803; 1915, **86**, I, 98; Zts. Schiess. Spreng. 1914, **9**, 394; J. C. S. 1914, **106**, ii, 673; Zts. ang. Chem. 1914, **27**, II, 654. For the Soc. anon des Celluloses Planchon method and apparatus for the estimation of nitrogen in nitrocellulose gasometrically, see F. P. 490948, 1919; abst. Chem. Ind. 1920, **3**, 221.

The conclusions reached by the investigator are as follows:

1. The general results indicated that the nitrometric estimation of nitrogen in nitrocellulose invariably gives too low results.

2. It was found that the interval of time which is allowed to elapse between the introduction of the cellulose nitrate and sulfuric acid into the nitrometer, and the shaking, has a great influence on the results, less so in the case of inorganic nitrates.

3. The most accurate results are obtained by using 15 cc. of 92.5%–94.0% sulfuric acid, and by allowing 15-30 minutes to elapse between the introduction of the nitrocellulose and acid into the nitrometer and the shaking. In this case, the error is about 0.7%, taking the total nitrogen as 100.

Stability Tests, sometimes also called "heat" and "fume" tests, are applied to explosives to determine their keeping qualities, which is their stability. Applied to the product in the course of manufacture, they are of value as indicating the extent to which purification has been carried, i. e., completeness with which those products have been eliminated which might induce decomposition, or cause spontaneous combustion. As cellulose and glycerol nitrates decompose but slowly at the ordinary temperature when properly prepared and purified, and samples of guncotton have been stored for years without serious deterioration, yet the sulfuric esters and other indefinitely characterized bodies formed in manufacture and which are extremely difficult to remove from the nitrocellulose, render accurate control of stability to be a necessary requisite for safe production. Before the value and accuracy of stability tests were established, the series of fatal explosions which resulted in attempts to produce guncotton in large amounts commercially, temporarily put a stop to its manufacture in various countries. It was not until F. Abel had proven the value of his "heat test," that it became possible to prepare nitrocellulose-containing explosives in large quantities with a reasonable amount of safety and uniformity. Although this test has many imperfections, it is perhaps to-day the most widely used single nitrocellulose stability test. Nearly all the stability tests evolved depend either upon the measurement of

TABLE CL

GIVING ANALYSES OF THE VARIOUS PRODUCTS OF NITROMETER DETERMINATIONS

Substance Used	Sulfuric Acid Per cent.	Interval Between Introducing Guncotton and Acid into the Nitrometer and Shaking	Substance Used Grams	Analysis of Gas			
				NO. Cc.	CO_2 and SO_2 Cc.	CO_2 Cc.	N_2 and N_2O Cc.
Dupont high nitrogen guncotton	96.8	None	0.51135	106.76	0.25	0.25	0.82
	96.8	None	0.50965	106.27	0.30	0.25	0.85
Guncotton	96.8	None	0.54865	111.81	0.64*	0.22	0.82
	96.8	None	0.5263	107.69	0.47*	0.17	0.80
Highly soluble nitrocellulose	96.8	None	0.54415	109.03	0.21	0.16	0.63
	96.8	None	0.53975	107.94	0.15	0.21	0.66
Blasting soluble nitrocellulose	96.8	None	0.55575	104.65	0.22	0.26	0.95
	96.8	None	0.55155	104.37	0.22	0.25	0.73
Pure sodium nitrate (Kahlbaum)	96.8	None	0.4513	117.70	0.11	....	0.48
	96.8	None	0.45265	118.09	0.03	....	0.50
Guncotton	99.87	None	0.52525	102.23	1.10	0.23	1.49
	96.8	20 Hours	0.5294	76.43	2.29	1.30	10.70
	92.5	None	0.5316	105.86	0.26	0.08	0.65
	92.5	1/4 Hour	0.5228	107.72	0.66	0.16	0.53
	96.8	17 Hours	0.4509	116.37	0.20	....	0.98
Sodium nitrate	99.87	None	2.867	95.08	0.45	....	0.75
Nitric acid dissolved in sulfuric acid	99.87	17 Hours	3.140	91.79	2.19	....	3.27

* Other results for the determination of carbon dioxide in the gas from guncotton were also obtained, but they were not added to th table, as the analyses were not completed. These results for a similar quantity of gas were: 0.57, 0.57, 0.40, 0.59, 0.56 cc.

TABLE CL. *Concluded*

Substances Used	Analysis of Residual Acid: N_2 and N_2O Evolved as Gas, Cc.	Analysis of Residual Acid: NH_3 Formed in Acid as Cc. NO	N_2 in Acid Used for Analysis Cc.	Nitrogen Calculated from Volume of Crude Gas Per cent.	Corrected Nitrogen Content Per cent.	Correction to be Added to Percentage o Nitrogen from Crude Gas
Dupont high nitrogen guncotton	0.59	1.16	0.39	13.21	13.44	0.23
	0.62	1.20	0.39	13.195	13.45	0.255
Guncotton	0.485	1.20	0.39	12.93	13.085	0.155
	0.50	1.13	0.39	12.96	13.14	0.18
Highyl soluble nitrocellulose	0.58	0.89	0.39	12.64	12.82	0.18
	0.59	0.94	0.39	12.62	12.81	0.19
Blasting soluble nitrocellulose	0.68	1.16	0.39	11.93	12.18	0.25
	0.635	1.12	0.39	11.965	12.18	0.215
Pure sodium nitrate (Kahlbaum)	0.38	0.15	0.39	16.382 = 99.48% NaNO₃	16.447 = 99.90% NaNO₃	0.065
	0.40	0.08	0.39	16.382 = 99.48% NaNO₃	16.459 = 99.97% NaNO₃	0.077
Guncotton	0.72	4.75	0.62	12.50	13.115	0.615
	2.06	8.83	0.39	10.71	12.9	2.19
		3.28	0.30	12.57		...
	0.45	0.98	0.30	13.04	13.14	0.10
	0.38	0.27	0.39	16.30	16.44	0.14
Sodium nitrate	0.67	0.07	0.62	...	...	...
Nitric acid dissolved in sulfuric acid	1.94	1.29	0.62	...	...	...

the volume of nitric oxide disengaged from a known volume of the sample in a determined period, and which are the so-called "trace-tests" in which the time taken to color a very sensitive reagent paper is noted, or the temperature is raised to the point where incipient or complete combustion ensues, as can be detected either by less sensitive reagents as litmus paper, or observable as fumes. A third subdivision may perhaps be made into the "quantitative tests," in which the products of combustion are analyzed, and the amount given off in a known period of time calculated. In the first class may be included the Abel, Guttmann, Hoitsema and Ordnance Department 115° tests; in the second class the Vieille, German Test at 135°, and in the third class the methods of Will, Bergmann and Junk, Obermüller, Thomas and Hess, all described herewith.[1,2,3,4]

Heat Tests (Including Other Trace Tests). The heat test is the simplest and most generally applied of all the stability tests. Although it is but a measure of the initial decomposition of the nitro-explosive and not always a true indication of stability, yet in most countries it has been adopted as a standard test which must be passed by nitro-explosives prior to acceptance. The potassium iodide-starch test, or as it is sometimes called, the "Abel heat test," or simply the "heat test," depends upon the fact that when a nitro-explosive is heated, oxides of nitrogen are evolved. These gases coming in contact with moist potassium iodide liberate iodine, and this in presence of starch gives a blue color reaction. The Abel test, however, is not a true test for

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[1] For "Methods of Testing Stability of Explosives in Various Countries," see R. Escales, Z. ges. Schiess. Spreng. 1910, **5**, 21, 72; abst. C. A. 1910, **4**, 1161, 1370. Exhaustive series of reports by a special commission appointed by 6th Int. Cong. Applied Chem. to investigate the subject. See A. Leroux, Bull. Soc. Chim. Belg. 1905, **19**, 243; M. Jacqué, Z. Schiess. Spreng. 1906, **1**, 395.

[2] W. Cullen, J. S. C. I. 1901, **20**, 8.

[3] Regulations for army Ordnance Service Pt. II, 1916. F. Abel, 2nd Memoir Phil. Trans. 1867, **157**, 181; J. C. S. 1867, **20**, 505; Phil. Mag. 1867, **33**, 545; Proc. Roy. Soc. 1867, **13**, 417; J. U. S. Service Inst. 1867, **10**, 417; Chem. News, 1867, **15**, 203; Poly. Centr. 1867, **33**, 283, 1186, 1414; Wag. Jahr. 1867, **13**, 329; Dingl. Poly. 1867, **185**, 148, 154; Chem. News, 1867, **14**, 250; Jahr. Chem. 1867, **20**, 912; Amer. J. Sci. 1867, (2), **44**, 288; Bull. Soc. 1867, (2), **7**, 527; Deut. Ind. Ztg. 1867, 202; J. prakt. Chem. 1867, **101**, 488; Les Mondes, 1867, **14**, 224; **15**, 689; Chem. Tech. Rep. 1867, **6**, II, 122; 1867, **6**, I, 120; Pharm. J. Trans. 1868, **9**, 386; Compt. rend. 1869, **69**, 105; Ann. Chim. Phys. 1870, **21**, 97. For discussion of above by A. Chariere, see Les Mondes, 1868, **16**, 143.

[4] J. U. S. Artillery, Sept.-Oct. 1903. A. Sy, J. A. C. S. 1903, **25**, 549.

nitrous acid,[1] for the iodine is liberated by a process of oxidation in accordance with the equation:

$$2KI + O + H_2O = 2KOH + I_2$$

This iodine liberation, however, is complicated by a further reaction:[2,3]

$$2KOH + I_2 = KI + KOI + H_2O.$$

This second reaction being reversible.

The test, in brief, consists in observing the time taken for the color to develop to a certain intensity when the explosive is heated under standard conditions. The test suffers, however, from being too sensitive and too easily interfered with by slight alterations in procedure. A quantity of 135×10^{-6} mgm. of nitrogen peroxide is sufficient to produce the standard tint in the heat test paper.[4] Unless the test is carried out under strictly defined conditions, results may be obtained which may lead to erroneous conclusions, as traces of substances in the explosive may be expelled in the heat test and thus affect the heat test paper. In consequence, a low result does not necessarily indicate deficiency in stability of an explosive. If a small figure is obtained in this low temperature test quantitative confirmatory tests—such as the Will or Bergmann and Junk tests for nitrocellulose—should be carried out[5] preliminary to arriving at a conclusion. Undoubtedly, by the application of the heat test, much experimental data can be produced to show the uncertainty of the test, and difficulty will be experienced in reconciling much apparently conflicting data. It must, however, be remembered as pointed out by B. Smart[1] that (1) in applying the Abel test to explosives the physical conditions must never be lost sight of, (2) with guncotton we have a solid fibrous substance containing water of constitution; (3) with nitroglycerol we are dealing with a liquid which does not readily permit the dissolved gas produced by the decomposition to be evolved; and (4) with gelatinized explosives we have solid products with only a limited surface containing substances which react with oxides of nitrogen, which may easily contain the accumulation of past decomposition and which may decompose or partially volatilize during preparation for the test. When these points are remembered the irregularities and discrepancies of the Abel test may be better understood.

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[1] B. Smart, J. S. C. I. 1913, **32**, 967; abst. C. A. 1914, **8**, 422; J. C. S. 1913, **104**, ii, 1080; Chem. Zentr. 1914, **85**, I, 501; Zts. ang. Chem. 1914, **27**, II, 211; Zts. Schiess. Spreng. 1914, **9**, 12. See also A. Egerton, J. S. C. I. 1913, **32**, 331. F. Lenze and B. Pleus, Zts. Schiess. Spreng. 1919, **14**, 297, 315; abst. Chem. Zentr. 1920, **91**, II, 107; J. S. C. I. 1920, **39**, 281-A, 468-A; C. A. 1920, **14**, 2418.

[2] F. Foerster and K. Gyr, Zts. Elektrochem. 1903, **9**, 1; abst. J. C. S. 1903, **84**, ii, 209, 352; J. S. C. I. 1903, **22**, 144; Chem. Centr. 1903, **74**, I, 311, 862; Jahr. Chem. 1903, **56**, 509.

[3] R. Taylor, J. C. S. 1900, **77**, 725; abst. J. S. C. I. 1900, **19**, 385; Chem. Centr. 1900, **71**, I, 844; II, 86.

[4] R. Robertson and B. Smart, J. S. C. I. 1910, **29**, 130; abst. C. A. 1910, **4**, 1807; Bull. Soc. Chim. 1910, **8**, 684; Chem. Zentr. 1910, **81**, I, 1650; II, 420; Jahr. Chem. 1910, **63**, II, 146; Wag. Jahr. 1910, **56**, I, 496; Zts. ang. Chem. 1910, **23**, 1963; Zts. Schiess. Spreng. 1910, **5**, 185, 208.

[5] In the case of guncotton with a high $CaCO_3$ content it is usual to remove the $CaCO_3$ by dilute acid and then thoroughly wash before heat test.

A special room, or preferably a small building, should be exclusively reserved for work in connection with this test and volatile solvents, acids, etc., should be rigidly excluded from the building.

According to the U. S. Ordnance method of testing guncotton, the heat test is carried out as follows: The sample should be pressed in a clean cloth or wrung in a wringer if it contains a large excess of water. The cake shall be rubbed up in the cloth until fine, taking care that it does not come in contact with the hands, spread out on clean paper trays, and dried in an air bath at 35°-43°, just a sufficient length of time to reduce the moisture to that amount which will give a minimum heat test, this amount being from 1.5%-2%. If, as sometimes happens in dry weather, the moisture has been reduced to less than 1.5%, the sample shall be placed in a moist atmosphere for a time not exceeding two hours, until the required moisture is obtained. The whole time of drying and making the test shall not exceed eight hours.

The dried sample for the heat test shall be weighed out in 5 test tubes, 1.3 gm. (20 grains) to each tube, so that a series is obtained covering the widest variation allowed for moisture. These tubes are standard, 5.5 in. long, $^1/_2$ in. internal diameter, and $^5/_8$ in. external diameter, closed by a clean cork stopper, fitting tightly, through which passes a tight glass rod with platinum holder for the paper. Corks are discarded after one test. The nitrocellulose is pressed or shaken down in the tube until it occupies a space in the tube of 1$^5/_8$ in. The test paper, about 1 in. in length and 3 in. wide, is hung on the platinum holder, and moistened on its upper half with a 50% solution of pure glycerol and water. The heating bath, carefully regulated at 65.5° ± 1° is placed so that a bright reflected light is obtained and the tube placed in the bath. Time is marked when the tube enters bath. As test continues, a slight film of moisture condenses on inside of tubes, and the line of demarcation between wet and dry test paper is kept abreast the lower edge of the moisture film. The first appearance of discoloration of the damp portion of the test paper marks the end of the test for each separate tube, the minimum test of any one of the five tubes being the heat test of the nitrocellulose. This discoloration is to be greater than that obtained at the same time by a blank test. The standard water bath holds ten tubes and is made long and narrow, to reduce to a minimum the heating of the upper portions of the tube. These tubes are immersed in the bath to a standard depth of 2.5 in.[1]

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[1] J. S. C. I. 1913, **32**, 967; abst. C. A. 1914, **8**, 422; J. C. S. 1913, **104**, ii, 1080; Chem. Zentr. 1914, **85**, I, 501; Zts. ang. Chem. 1914, **27**, II, 211; Zts. Schiess. Spreng. 1914, **9**, 12.

The British method[2] of carrying out the heat test differs in some essential particulars from the above. The test requires a spherical copper water bath of about 8 in. diameter with an aperture of about 5 in., fitted with a loose copper lid about 6 in. in diameter, this resting on a tripod 14 in. high. The whole is surrounded by a thin sheet-copper screen, being heated from underneath by means of an Argand gas burner or Berzelius spirit lamp with copper chimney. The water-bath lid is pierced with 7 holes, one to receive a thermometer and the remaining 6 holes for test tubes containing the material to be tested. A potassium iodide-starch paper and a standard tint paper are also specified. The applications of this test are as follows:

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[1] The weak points in this test as summarized by A. Sy (J. A. C. S. 1903, **25**, 550) are as follows: In cases of the decomposition of the sample during the test, it shows only the beginning and not the continuation of the decomposition, it being more important to know how decomposition proceeds than when it begins. Traces of unstable nitro compounds would show a nitrocellulose or powder in which they are found by this test to be bad; yet such traces might not cause a decomposition of the explosive if stored under ordinary conditions. Traces of solvent left in the powder affect the test. The test may be masked by certain substances as mercury salts, as the chloride, carbonates, alkalis, amine, ethyl acetate, acetone, oils, vaseline and aniline, which may be added to the explosive for that purpose. Explosives containing masking substances are not accepted by the Ordnance Department. The test is affected by the condition of the sample, size of grains, whether recently prepared for testing or exposed to air, moisture in the air and slight differences in test papers.

[2] The originally described process provides for an elaborate wooden cupboard to hold the apparatus, so that in event of an explosion the effects might be confined. Complete directions for performing this test may be found in "Regulations for Army Ordnance Service," Wyman & Sons, Publishers, 1908, II, 162–167.

For illustrations of apparatus used in this test, see Appendix VI, Regulations for English Ordnance Service, part 2, reproduced in Allen Comml. Organic Analysis, 1910, **3**, 596.

Guncotton, Tonite, Schultze Powder, E. C. Powder, etc. The sample is prepared by removing from the center of the block or cartridge, by gentle scraping or rasping, and if necessary, further reducing to powder by rubbing through the fingers or a sieve with a clean, stiff-bristle brush. The fine powder thus obtained is spread out in a thin layer upon a paper tray 6 x 4.5 in., which is placed upon a wire gauze in the water oven, the temperature of which is kept as uniformly near to 49° as possible. The sample is allowed to remain at rest in the oven for fifteen minutes, the door of which is meanwhile left open. After the lapse of fifteen minutes the tray is removed, exposed to the air for two hours, the sample being at some point within that time rubbed upon the tray with a brush or the hand in order to reduce it to a fine and uniform state of subdivision. In applying the test the water bath is first filled to within 0.25 in. of the top, the thermometer inserted through a hole on one side of the water-bath cover, to a depth of 2.5 in., measured from the lid, the water being maintained at a temperature of 76.7° during the progress of the tests. When the correct temperature has been obtained, 1.3 gm. of the sample is weighed out, placed in one of the test tubes, and gently pressed down until it occupies not more than 1.3 in. in the tube. A test paper is fastened to the hook of the glass tube, moistened by touching the upper edge with a drop of a mixture of equal amounts of distilled water and glycerol, the quantity of liquid used being only sufficient to moisten the upper half of the paper. The cork to which the rod and paper is attached is then inserted into the tube, and the latter placed into the bath to a depth of 2.5 in., measured from the cover. The test paper is first placed near the top of the tube, but not touching the cork, until after the tube has been immersed five minutes. A ring of moisture will by this time have deposited upon the sides of the test tube, slightly above the cover of the bath. When this appears, the glass rod is then lowered until the lower margin of the moistened portion of the paper is on a level with the ring of moisture in the tube. The paper is closely observed, and when a brown line appears at the line of demarcation between the moist and dry portions of the paper, which is equal in intensity to the line on the standard tint-paper, the time is observed and the test is complete.

(A standard tint is made as follows: 0.48 gm. of the finest yellow ochre, 0.2 gm. raw umber and 5 gm. of fine, white gum arabic are all separately ground to an impalpable condition and then thoroughly shaken with 100 cc. cold water. After standing for 1 hour a stylographic pen is filled from the center of the suspension and with it lines not less than 0.5 mm. or more than 1 mm. wide are ruled across filter paper.)[1] In carrying out the heat test the procedure of the British Home Office differs in many details from those of the British War Office. Moreover, there is a tendency for private explosive laboratories to evolve slightly altered methods for their individual use. In consequence a joint committee of the Home Office, Admiralty, War Office and Explosives firms has been set up to consider the question of the heat test generally, and in their first report (1914) have recommended that the test should be carried out under strictly uniform conditions. It is recommended that the test tubes should conform to the following specification: Weight 10–11.5 gm. capacity 20–22 cc., length 5.5 inches. When the tubes are subjected for three hours to a steam pressure of 50 lbs. per sq. inch and then air-dried, they should show practically no cloudiness (c. f. with a standard tube). The test tube has 3 marks etched on it, 3, $3^{3}/_{4}$ and 5 inches from the bottom. The lowest mark indicates the depth the tube is to be inserted in the bath, the middle one indicates the level of the lower moistured part of the test paper, and the top line the level of the lower side of the rubber stopper which is used for the tube. It is also recommended that the test paper at the commencement of the test should be placed in its permanent position as indicated by the etching on the tube. Moreover, as light influences the development of the tint on the heat test paper, it is suggested that the heat test tube should be covered with a black cap during the test, and this cap should only be removed shortly before the end of the test.

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[1] The standard tint paper is prepared by diluting caramel with water to such an extent that when further diluted 100 times the tint produced matches that from Nessler's reagent in 100 cc. water containing 0.000235 gm. ammonium chloride. With this caramel solution lines are drawn on strips of well-washed filter-paper with a quill pen, the paper being cut into strips same size as the test paper described in the previous note after drying. Only those strips are used in which the brown line has a breadth of from 0.5–1.0 mm. This paper should be protected the same as the iodide paper.

For nitrocellulose pulp the following procedure is recommended: The pulp is pressed between six thicknesses of filter paper and 5 gm. (approximately) of the pulp, dried at 50° on an aluminium tray for 15 minutes. The dried material is sieved under specified conditions and exposed to the atmosphere for 4 hours and 1.30 gm. weighed out. This sample is pressed down gently in the heat test tube to a height of 3 cm. and then subjected to the test in the usual way. The exposure for 4 hours gives a nitrocotton with a moisture content of about 1.5 (see hygroscopic moisture). In a very dry material a high heat usually results owing to the drying of the test paper. As material with much higher moisture content than above also tends to give a high heat test owing to the water condensing on the upper portion of the tube during the test and thus absorbing oxides of nitrogen.

Compressed guncotton is first broken up and pieces scraped with a horn spatulum from the center of the slab. These particles are stirred for 15 minutes with cold distilled water, which is then decanted and the material treated as in the case of pulp.

Cordite, *Ballistite*, and similar partially or wholly gelatinized preparations, are tested as follows: If the sample is in the form of small flakes or grains, as in the U. S. 0.30-caliber, and other shoulder-arm powders, 1.6 gm. are weighed out into a test tube, but if, as in the case of cordite and larger caliber powders, the grains are larger, they must first be broken up and ground. From each of the pieces selected for the test, pieces 0.5 in. long are cut, and in the larger sizes the pieces further subdivided. The cut pieces are then passed through the mill, the first portion rejected on account of possible presence of iron or other extraneous matter. The ground portion is then placed on the top sieve of the nest and sifted, the portion which passes through the top sieve, but is intercepted by the second, is taken for the test.[1]

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[1] If the nitrocellulose is too hard for the mill, it may be softened by exposure to acetone vapor, or reduced to the required fineness by means of a coarse rasp. If the acetone vapor renders the sample too soft, it may be

The English Home Office Instructions for applying the test are as follows: The thermometer is so adjusted in the water bath as to be inserted into the water 2.75 in. below the water bath lid, the water being maintained at the uniform temperature of 82.2°. An iodide paper is attached to the hook on the glass rod, so that when inserted in the tube it will be in a vertical position, being moistened with 50% glycerol as previously described. The cork, with the rod and test paper attached, is inserted into the tube and the position of the paper so adjusted that its lower edge is about half way down the tube, the latter being then inserted through one of the holes in the cover of the water bath to such a depth that the lowest portion of the moistened paper is about 0.6 in. above the surface of the cover. When a faint brown tint, equal in intensity to the brown line drawn on the standard paper, makes its appearance at the line between the wet and dry portions of the test paper, the test is complete. With cordite, the English Home Regulations specify that the time between the insertion of the test tube into the bath at 82.2° and the completion of the test must not be less than fifteen minutes, and no new cordite is accepted by the War Department from contractors unless it meets these requirements.[1]

Samples of smokeless powder should be cut into slices 0.02 inch thick and 1.3 gm. of a sample which has been exposed to the air for 12 hours used for the test.

Gelatinized explosives, according to the 1914 Departmental report, should be tested as follows: A sample weighing 3.2 gm. is weighed out and ground up with 6.5 gm. of French chalk in a Wedgwood mortar, the grinding being carried out at first with a squeezing and then with a circular movement of the pestle. With

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restored to the desired degree of hardness by simple elimination of solvent by exposure to the air. The sifted material should always be dried at not to exceed 61°, where the volatile matter in the sample exceeds 0.5%. Explosives consisting of both gelatinized and ungelatinized nitrocellulose may be reduced to powder by first softening with ether-alcohol vapor at about 35°, or usually more easily by the use of a coarse rasp. See W. Cullen, J. S. C. I. 1901, **20**, 8.

[1] No new cordite is accepted by the War Department from contractors which does not satisfactorily stand a heat test of thirty minutes, at 82.2°, although the test is carried out with less sensitive papers than those prescribed by the Home Office. Cordite already issued to the service is tested at 71.1°, it being considered serviceable if it stands the test for eight or more minutes, and unserviceable if below eight minutes, and more than four minutes.

blasting gelatin the squeezing movement is carried on for $1^1/_2$ minutes, with gelatin dynamite for 1 minute, and with gelignite for $^1/_2$ minute, the circular movement being in all cases maintained for $^1/_2$ minute, after which the mass should be homogeneous in appearance. The mixture is gently pressed down in the test tube to a height of 5 cm.

The committee found that different qualities of French chalk give different results when used for heat test purposes, but they were unable either to find a substitute or propose a definite specification. As a tentative measure they suggest the following:

(1) It must not contain more than 5% of moisture.

(2) Its bulk must be such that 50 cc., without ramming or tapping, weigh 23.5 ± 1 gm.

(3) It must pass a sieve composed of wire 0.075 mm. in diameter and having 6400 meshes to the square centimeter, no rubbing being used.

(4) It must contain less than 0.1% of soluble alkali calculated as $CaCO_3$.

(5) When warmed with hydrochloric acid it must give off at least 0.25% of carbon dioxide, but not more than 1%.

(6) It must not absorb more than 0.5% of moisture when exposed for 24 hours to a saturated atmosphere at 15°-20° after being dried at 100°.

With nitroglycerol approximately 2 cc. of the explosive are placed in heat test tubes. It is filtered through 3 filter papers to remove moisture and the quantity approximately judged by an etched mark on the test tube, the test being carried out at 71.1° in duplicate.

If nitroglycerol is mixed with a relatively large amount of silica wool, a considerably lower heat test is obtained than if the above procedure is adopted. This second method exposes a large surface of the nitroglycerol and the result obtained is probably nearer to the true heat test. Unless a large surface of liquid is exposed, the nitroglycerol dissolves much of the nitrogen peroxide as formed. The heat test result thus appears high. That nitroglycerol even when pure should give a comparatively low heat test is in conformity with the fact that its rate of decomposition, as measured by more exact methods, is nine times as fast as that of nitrocellulose. "Dynamite and other nitroglycerols in which the latter is readily removed by water are treated as follows: 13 gm. of the material are evenly pressed down with a glass rod on a filter paper supported by a $5^1/_2$ cm. glass funnel. The funnel is then placed in a heat test tube and filled with water. 2 cc. of the displaced nitroglycerol are collected (free from water) and then heat tested in the usual way. Carbonite and similar friable preparations from which the nitroglycerol cannot be readily extracted with water are directly heat tested without previous treatment.

As the test is extremely sensitive and much influenced by the method of preparation of the heat test papers, it is usual to have the latter made under official supervision.[1] The potassium iodide should before use be recrystallized three times from 95% ethyl alcohol and all precautions should be taken to obtain the pure crystals. Maize starch in the form of corn-flour is to be employed and it is to be thoroughly washed with distilled water before use. 3 gm. of the starch are suspended in 30 cc. distilled water and then poured into 220 cc. of freshly distilled water in a Jena glass flask. The whole is boiled for 5 minutes. The resulting mixture is poured into a solution of 1 gm. of potassium iodide in 250 cc. of distilled water, well mixed and the whole allowed to stand overnight in a dark room. The clear solution is then siphoned off and immediately used for dipping. Sheets of special filter paper (see below) are passed singly through this solution. The paper is then hung up to dry and a clean glass rod passed down each side to remove the excess of solution, after which the drying is completed in a warm room. When dry the ends of the paper which are undipped are cut off and rejected. In addition a small strip round the edges is also removed. The remainder is cut into small strips 2 cm. long and 1 cm. wide and preserved for use in brown glass bottles in the dark. The cutting up is done in a special room (partly darkened and used only for this operation) and the operator wears clean cotton gloves. The special paper used should as nearly as possible comply with these specifications:

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[1] The standard test paper is prone to deterioration, and its condition should be frequently ascertained by the following test: Place a drop of dilute acetic acid by means of a glass rod on a strip of the paper being tested. If the paper is in good condition no discoloration takes place. If the acid produces a brown or bluish coloration the paper is to be rejected. If the paper is unserviceable the discoloration appears at once, any discoloration appearing some time afterwards being disregarded.

(1) To consist of pure normal cotton cellulose of strong resistant quality and free from every loading or sizing.

(2) To have a smooth white surface both sides being as nearly alike as possible.

(3) The average length of the fibers to be 2 ± 0.5 mm.

(4) The thickness to be 1.8 ± 0.2 mm. (Cf. Smith's patent fixed pressure micrometer).

(5) The last treatment in its preparation to be a thorough washing with distilled water, and subsequent air drying in a pure atmosphere.

(6) To be free from all impurity, particularly acids, chlorine and peroxides.

(7) The loss of weight when boiled for 1 hour with 3% caustic soda solution not to exceed 7.5%.

(8) It is not to produce more than 1.25% of its weight of cuprous oxide when heated to 100° C. for 15 minutes with Fehling's solution diluted with its own volume of boiling water.

(9) The sheets are to measure 50 cm. and are to be packed in hermetically sealed tin cases holding 100 sheets each.

According to C. Storm,[1] exposure to light does not appear to affect the papers if moisture and deleterious fumes are excluded, although it is probable that freshly made papers are more sensitive to the action of light than old papers.

The test is masked by traces of mercuric chloride (see topic Mercuric Chloride in Guncotton), also by the presence of various solvents such as ethyl alcohol and ethyl acetate. Other compounds, such as peroxides, reduce the time of the test, while acetone has little effect, only increasing it slightly. The presence of various stabilizers, such as diphenylamine, various amines and mineral jelly, also generally increase the time of the test.

The Abel heat test is really a test for detecting the presence of small quantities of nitrogen oxides by the aid of potassium iodide starch paper. Other trace tests have been devized in which the potassium iodide is replaced by other substances. In Germany zinc iodide replaces the potassium iodide and gives a still more sensitive test. In Spain the dipping solution for the paper consists of water (100 cc.), starch (5 gm.), zinc iodide (2 gm.) and zinc chloride (20 gm.), and this replaces the potassium iodide. Thus, in Guttman's test it is replaced by diphenylamine and dilute sulfuric acid; in J. Moir's test[1] it is replaced by naphthylamine, sulfanilic acid and acetic acid (Ilosvay's reagent); and in G. Spica's test[2] by the very sensitive *m*-phenylene diamine and cane sugar.

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[1] C. Storm, J. Ind. Eng. Chem. 1909, **1**, 802; Boll. chim. farm. 1914, **53**, 736; abst. C. A. 1910, **4**, 514; 1916, **10**, 1970; J. S. C. I. 1910, **29**, 117; Chem. Zentr. 1910, **81**, I, 1806.

A. Egerton[3] uses a similar reagent to Moir, but replaces the paper by a glass receptacle for the reagent. Some of these tests will be referred to in more detail.

The Guttmann Stability Test.[4] Consists in employing filter paper wetted with a solution of diphenylamine[5] in sulfuric acid,[6] the test being applied in the following manner: 1.5 gm. of the cellulose nitrate is placed in the regulation size and form of test tube. Strips of well-washed filter paper, 25 mm. wide, are hung on a hooked glass rod in the tube. A drop of the diphenylamine solution is taken up by means of a clean glass rod, and the upper corners of the filter paper are touched with it, in such a manner that when the drops run together about a fourth of the filter paper is moistened. This is then put into the test tube, and this again into the water bath, which has been heated to 70°. The heat-test reaction should not appear in less than fifteen minutes, and will begin by the moist part of the paper acquiring a greenish yellow color, and from this moment the paper should be carefully watched.[1] After one or two minutes a dark blue mark may suddenly appear on the dividing line between wet and dry paper, which is the point which is to be looked for.[2]

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[1] See A. Egerton, J. S. C. I. 1913, **32,** 331; 1914, **33,** 113.

[2] Revista, Aug. 1897. Atti. del Reale Inst. di Sci. See J. Zigall, Third Intl. Cong. Appl. Chem.

[3] J. S. C. I. 1913, **32,** 331; 1914, **33,** 113; abst. C. A. 1914, **8,** 1504; J. C. S. 1913, **104,** ii, 534; 1914, **106,** ii, 390; Chem. Zentr. 1913, **84,** II, 908, 2063; 1914, **85,** I, 1379; Meyer Jahr. Chem. 1913, **23,** 363; Zts. ang. Chem. 1914, **27,** II, 211, 581; Zts. Schiess. Spreng. 1913, **8,** 390.

[4] J. S. C. I. 1897, **16,** 283, 293; Zts. ang. Chem. 1897, **10,** 233, 265; 1898, **11,** 1103; 1900, **13,** 592, abst. J. S. C. I. 1899, **18,** 174; Rev. Phys. et Chim. 1896–1897, **1,** 409; Mon Sci. 1898, **51,** 37; 1899, **53,** 148; 1900, **55,** 831; Chem Centr. 1897, **68,** I, 1185, 1186, 1899, **70,** I, 70; Jahr. Chem. 1897, **50,** 1064; 1898, **51,** 1380; 1900, **53,** 849; Meyer Jahr. Chem. 1897, **7,** 300; Wag. Jahr. 1897, **43,** 487; 1898, **44,** 383; 1900, **46,** I, [illegible]. C. Kullgren, Zts. Schiess. Spreng. 1912, **7,** 153; abst. J. S. C. I. 1912, **31,** 459, finds when using a diphenylamine test paper, that if guncotton of low heat test (3–4 mins.) be heated continuously for 6–14 days at 45° C., the heat test rises to 11–12 minutes. He considers that this points to the fact that unstable bodies in the guncotton are not immediatley decomposed into nitrogen peroxide, but pass through one or more intermediate stages of decomposition.

[5] G. Spica (Revista, Aug., 1897) proposes to impregnate the paper with *m*-phenylenediamine hydrochloride and cane-sugar, but as the reagent is much more sensitive than potassium iodide and starch, it has not been more extensively used.

[6] 0.10 gm. diphenylamine crystals are placed in a wide-necked flask, stoppered, with 50 cc. dilute sulfuric acid (10 cc. acid, 40 cc. water) and placed on a water bath at 50°–55°. This temperature will cause the diphenylamine to melt and at once pass into solution in the sulfuric acid. The flask is then removed, shaken, cooled, 50 cc. concentrated glycerol added, and the finished reagent kept in the dark.

C. Hoitsema[3] uses a similar indicator (diphenylamine and

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[1] This test has been adopted by the Belgian military authorities and is used elsewhere, but J. Thomas (Zts. ang. Chem. 1898, **11**, 1027), H. Aspinwall (J. S. C. I. 1902, **21**, 687) and G. Spica (Revista, Aug., 1899) have found it unsatisfactory. F. Nathan (J. S. C. I. 1901, **20**, 10) finds the test fails when testing volatile explosives such as nitroglycerol, the latter being decomposed by the sulfuric acid on the paper. C. Hoitsema (Zts. ang. Chem. 1889, **2**, 705) heats the explosive at a constant temperature for fifteen minutes, and then aspirates the volatile products of decomposition by means of a current of carbon dioxide, through glass wool moistened with Guttmann's diphenylamine solution. This operation is repeated, lowering the temperature each time by 10°, until a temperature is reached at which no volatile decomposition products come over which give a color reaction with diphenylamine, this being taken as the point at which decomposition ceases. This test is exceedingly sensitive.

[2] W. Dreger (Zts. Schiess. Spreng. 1909, **4**, 123) determines diphenylamine, based upon the fact that in alcoholic solution it reacts with bromine to form tetrabromodiphenylamine:

$$(C_6H_5)_2NH + 8Br = (C_6H_3Br_2)_2NH + 4HBr$$

This bromo-derivative is insoluble in water, sparingly soluble in alcohol, readily soluble in benzene, xylene, chloroform, and ethyl acetate, especially on warming; it melts at 102°, and crystallizes in reddish needles having a silky luster. For the determination of diphenylamine in the commercial product, the sample is dissolved in alcohol, or if already in ethereal solution, the ether may be driven off by adding alcohol and warming. Excess of bromine is then added, drop by drop, with constant stirring. The solution is next mixed with twice its volume of water and the whole boiled until the alcohol and excess of bromine are driven off and the bulk is reduced to one-half—constant stirring is needful. The precipitate of tetrabromodiphenylamine is transferred to a funnel, or Gooch crucible, connected to a water pump, and washed with warm water to remove the last traces of alcohol and bromine, and lastly dried at 98°–100° until of constant weight. Smaller quantities may be estimated by evaporating to dryness in a previously weighed glass vessel. If it be desired to determine the diphenylamine contained in gelatinized nitrocotton, the nitro-compound is gradually decomposed by means of soda lye in a capacious flask. The flask is closed by a doubly perforated stopper fitted with a stoppered funnel, and a bent tube attached to a condenser, which communicates with a suitable receiver. The free diphenylamine and any camphor that may be present are carried into the receiver which contains ether. The distillate is well shaken with common salt; the ether completely dissolves the diphenylamine and any camphor, and the determination is then completed as before indicated.

[3] Zts. ang. Chem. 1899, **12**, 705; abst. Wag. Jahr. 1899, **45**, I, 423; J. S. C. I. 1899, **18**, 857; Chem. Centr. 1899, **70**, II, 547; Jahr. Chem. 1899, **52**, 1304; Mon. Sci. 1899, **53**, 826; Tech. Chem. Jahr. 1899, **22**, 146; Meyer Jahr. Chem. 1899, **9**, 300. S. Jannopoulous (Zts. Schiess. Spreng. 1906, **1**,

sulfuric acid), but carries out the test differently. The explosive is heated in a thermostat for 15 minutes at a particular temperature and the volatile products of decomposition are then removed by a current of carbon dioxide. A blue color shows the presence of oxide of nitrogen. The test is repeated, reducing the temperature 10° each time until a point is reached when there is no reaction. G. Spica prepares his test paper by dipping Berzelius paper in a 0.1% aqueous solution of *m*-phenylenediamine hydrochloride. The solution should be kept in the dark, preferably over calcium chloride. The paper is moistened before the test with an aqueous solution of sugar (10%). The test is carried out at 66°–67° in the case of guncotton and nitroglycerol, and 71° in the case of ballistite. A blank test must always be carried out by heating an empty tube in which the paper is suspended; this procedure is necessary owing to the extreme sensitiveness of the test. A. Egerton's reagent[1,2,3,4] consists of (1) 5 cc. of 0.1 gm. naphthylamine in 100 cc. of 0.01/N acetic acid, 5 cc. of 0.5 gm. sulfuric acid in 100 cc. of 0.001/N acetic acid and 10 cc. of glacial acetic acid; (2) a nearly saturated solution of dimethylaniline in glacial acetic acid. The apparatus used gives a small, but definite surface which absorbs nitrogen peroxide and colors to a certain tint, depending on its concentration. The apparatus consists of two small discs 1.3 cm. diameter, one of opal and the other of clear glass, cemented together, the clear glass disk having a hole 0.5

349; abst. C. A. 1907, **1**, 105) has carried out an investigation for the purpose of ascertaining the effect which the solvents or gelatinizing agents present in smokeless powders exert on the Guttmann-Sparre test, using the diphenylamine paper, and the official German test, using the zinc-iodide-starch paper as the indicator of decomposition. A nitrocellulose smokeless powder was used in one set of experiments and a nitroglycerol smokeless powder in the other. Samples were heated to a temperature of 35° to 38° for four days. They were then tested side by side with fresh samples. With nitrocellulose powders the Guttmann-Sparre test gave an increased resistance of 6.5 to 7 minutes for the preheated samples over the fresh samples, and the official German test gave an increased resistance of 0 to 15 minutes for the preheated samples over the fresh samples. With the nitroglycerol powders only the Guttmann-Sparre test was used, and this gave a diminished resistance of 5 to 71 minutes for the preheated samples as compared with the fresh samples.

[1] The author is unaware of the delicate nitric acid reagent 9.10-monooxyphenanthrylamine, A. Schmidt and H. Lumpp (Ber. 1910, **43**, 794) having as yet been tried in this connection. See J. Strauss, Proc. U. S. Nav. Inst. 1910, **36**, 929.

[2] J. S. C. I. 1913, **32**, 331; abst. C. A. 1913, **7**, 2474.

[3] J. S. C. I. 1913, **32**, 112; abst. C. A. 1914, **8**, 1504.

[4] B. Smart, J. S. C. I. 1913, **32**, 967.

into the water bath, which has been heated to 70°. The heat-test reaction should not appear in less than fifteen minutes, and will begin by the moist part of the paper acquiring a greenish yellow color, and from this moment the paper should be carefully watched.[1] After one or two minutes a dark blue mark may suddenly appear on the dividing line between wet and dry paper, which is the point which is to be looked for.[2]

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[3] Zts. ang. Chem. 1899, **12**, 705; abst. Wag. Jahr. 1899, **45**, I, 423; J. S. C. I. 1899, **18**, 857; Chem. Centr. 1899, **70**, II, 547; Jahr. Chem. 1899, **52**, 1304; Mon. Sci. 1899, **53**, 826; Tech. Chem. Jahr. 1899, **22**, 146; Meyer Jahr. Chem. 1899, **9**, 300. S. Jannopoulous (Zts. Schiess. Spreng. 1906, **1**,

utes, for immediate use; under 10 minutes, to be destroyed.

The method proposed by the author is a modification of the test introduced by Sy. This consists in heating the sample of nitrocellulose (4 gm.) at a temperature of 115° for several days, for a period of eight hours per day, and determining the daily loss in weight.[1] The latter, taken in conjunction with the time of heating, is an index of the stability of the compound. For purposes of factory control this test has the disadvantage of being rather prolonged, and the author has modified it as follows: The sample to be tested is heated at 130°-140° C., and weighed after successive periods of heating of two hours duration. Nitrocellulose when dried to constant weight at 50°-60° C. still retains a certain percentage of moisture which is only driven off at temperatures above 100°, or by prolonged exposure, *in vacuo*, over sulfuric acid. It is important that this last trace of moisture should be got rid of before beginning the test proper. From 2-3 gm. of nitrocellulose are placed in a glass dish provided with a light, well-fitting cover to prevent absorption of moisture during weighing. The sample is heated to constant weight at 50°-60° and afterwards for ten minutes at 130° to drive off the last trace of moisture, and then weighed.[2] It is kept for two hours at a temperature of 130°-140°, cooled in a vacuum desiccator over sulfuric acid, and the loss in weight rapidly determined on a Curie balance. This process is then repeated some fifteen times further. The results are calculated on the basis of the loss in mgrm. per gm. of nitrocellulose taken, and these are the figures which appear in the subjoined tables. In general, the samples are heated with free access of air. Should it be desired, however, to study the decomposition in the presence of the products of decomposition, the glass weighing vessel can be enclosed in another, provided with a cover fitting air-tight by means of a rubber ring and spring. In the author's experience it is only when the nitrocellulose is unstable, that the presence of the products of decomposition accelerates the rate of decomposition. Standard stable samples of nitrocellulose are prepared by careful purification in the laboratory, and the factory output is checked against these as a standard of comparison.

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[1] M. Jacqué, Zts. Schiess. Sprengs. 1906, 1, 178, 207, 395; abst. J. S C. I. 1906, 25, 1117; Mon. Sci. 1907, 66, 271.

[2] A. Carneiro (Zts. Schiess. Sprengs. 1909, 4, 29; abst. J. S. C. I

Italy. G. Spica's report states that the heat test of nitrocellulose (1.3 gm.) is carried out at 66° to 67°, and should not be below 15 minutes, while nitroglycerol powders (3.25 gm.) ground and sifted through a 0.4–0.5 mm. sieve, should not show a test of less than 12 minutes at 71°.

In order to unify the methods of testing the stability of explosives, a committee was appointed at the Sixth International Congress of Applied Chemistry (1906).[1]

R. Robertson and B. Smart[2] have carried out an extensive study of the heat test and although they admit that there are points in connection with the Abel test which sometimes render it difficult to interpret the results obtained, yet in the majority of cases much information on the intrinsic decomposition of explosives may be observed. Their conclusions as tabulated below, unless otherwise stated, refer to fully purified non-gelatinized guncotton and nitroglycerol. From the experimental results obtained and knowing the rate of decomposition of an explosive, they have deduced a formula from which the heat test of an explosive may be calculated, on the assumption that only a process of decomposition with formation of nitric peroxide goes on during the test. The equation found is:

$$T = \frac{KV}{Q} \log \frac{r}{r + \frac{Q^2}{KV^2} - \frac{QrT}{KV}}$$

where *r* is the rate of rise in the concentration of nitric peroxide in the heat-test tube due to the decomposition of the explosive—

1909, **28**, 162) has made some experiments on the addition of diphenylamine to smokeless powders, as regards its effect upon the heat test. One gm. of the nitrocellulose powder was taken for the tests, which were carried out at a temperature of 80° C. In the case of nitroglycerine explosives the temperature was 70° C. The nitrocellulose powders having an original heat test of 9 to 11 minutes showed a drop in heat test of $^1/_2$ to 3 minutes after the addition of 1% of diphenylamine. The nitroglycerol explosives of 18 and 29 minutes heat test showed a drop of 1 to 4 minutes under similar conditions. After heating for 72 hours at 38° C., similar nitrocellulose powders showed a rise in heat test of 3 to 5 minutes, while the same samples containing diphenylamine showed a rise of only about $^1/_2$ to 1 minute. A similar treatment of nitroglycerine explosives gave a drop in heat test of 4 to $10^1/_2$ minutes in the untreated explosive and 9 to $12^1/_2$ minutes in the same samples containing diphenylamine. The author concludes that diphenylamine cannot be considered as a stabilizer for smokeless powder.

[1] See Zts. Schiess. Spreng. 1912, **7**, 435; abst. C. A. 1913, **7**, 701.

[2] J. S. C. I. 1910, **29**, 130; abst. C. A. 1910, **4**, 1807; Zts. Schiess. Spreng. 1010, **5**, 185, 208.

which may be experimentally determined by the formula

$$\left.\begin{array}{l} Q = 135 \times 10^{-6} \\ K = 31 \times 10^{-6} \end{array}\right\} \text{depends on the heat-test paper}$$

V = the unoccupied volume of the test tube (18 cc.)

r = the rise in concentration of nitrogen peroxide in the heat-test tube, due to decomposition of explosive. This can be experimentally determined.

For good guncotton, $\log r = 0.06021t - 10.6928$ if allowance is made for the log in the time of the test due to the fact that initially the guncotton is colder than the bath.

The results of R. Robertson and B. Smart's work have been summarized by them as follows:

(1) When Abel heat-test papers are exposed to an unlimited quantity of air containing nitric peroxide, the time required to produce a standard tint is inversely proportional to the concentration of nitric peroxide.

(2) For the standard heat-test papers as prepared at Waltham Abbey, the product of time in minutes by the concentration in milligrams of nitric peroxide per cubic centimeter is 31 x 10^{-6}.

(3) The total quantity of nitric peroxide absorbed by one of these test papers in coming to standard tint is 135 x 10^{-6} mgm.

(4) It is possible to calculate the heat test of an explosive when the rate of decomposition of which at a given temperature is known.

(5) The calculated heat test of guncotton at various temperatures and with varying quantities agrees well with the experimental results.

(6) This agreement taken in conjunction with many other experiments, serves to show that in the case of guncotton the Abel heat test represents the decomposition during the test of the guncotton itself, and is not due to dissolved impurities.

(7) When guncotton is to be heat-tested it is necessary to "condition" it. Very dry guncotton gives a high test, owing to the drying of the test paper, whereas wet guncotton gives a high test, owing to the excess of water which condenses in the test tube, absorbing considerable of the nitric peroxide.

(8) Since the heat test of a guncotton is but a measure of its initial decomposition, the test cannot safely be regarded as an

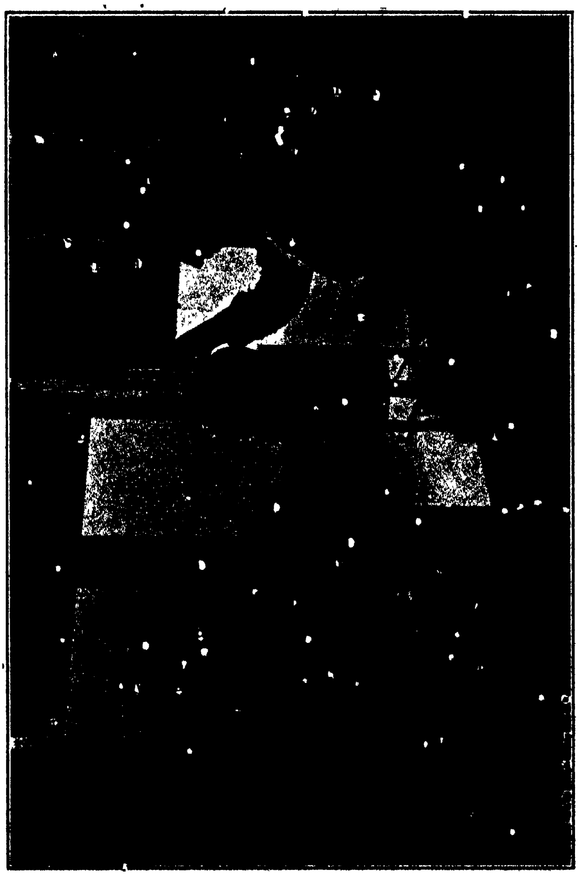

FIG. 288.—ABEL HEAT TEST APPARATUS

absolute determination of its stability. Under the Will test, non-volatile catalyzers may not give rise to an abnormal rate of decomposition until after 15–30 minutes at 135° have elapsed, which at 77° would correspond to much more than the actual duration of the heat test.

(9) When nitroglycerol is heat-tested in the normal fashion, the test obtained is very much higher than would be expected from the known rate of decomposition of nitroglycerol, but the calculated test is supported when the nitroglycerol is comminuted on specially purified silica wool.

(10) The solubility of nitric peroxide is so marked that at lower temperature the observed results were mostly too high.

(11) As ordinarily heat-tested, the time represents merely the solution pressure of nitric peroxide in the nitroglycerol.

(12) When small quantities of guncotton are added to nitroglycerol, the heat test rises, owing to the lowering of the solution-pressure of the nitric peroxide in the nitroglycerol, or to the increased viscosity of the liquid.

As soon as sufficient guncotton is added to break up the liquid meniscus, the heat test falls rapidly, owing to the comminution of the nitroglycerol. On account of the felting of the fine fibers, the comminution of the nitroglycerol is never so perfect in pastes as it is when the nitroglycerol is spread out on silica wool.

(13) When guncotton containing sulfuric esters is mixed with nitroglycerol the ester readily accelerates by catalysts, the decomposition of the latter, and low heat tests result.

Fume Tests (Stability). The Abel and various other trace tests already referred to are at most only of a qualitative nature. A large amount of experimental work has been carried out in order to obtain a better idea of the volatile products produced when nitrocellulose is heated at various temperatures below its explosion-point under standard conditions. As early as 1879, P. Hess[1] heated nitrocellulose in a tube to 70°, and by means of a current of air, the volatile products were aspirated into a dilute potassium iodide solution. Four colorimetric readings of the starch-iodide solution were made, as well as a record taken of the time of heating. O. Silberrad[1] also heated explosives to 70°. He used, however, unground smokeless powder and restricted the quantity of air. To make the test quantitative he proposed a measurement of the gas evolved or a measurement of the contraction due to the absorption of the oxygen. These tests require a very long time for their execution, if an appreciable amount of decomposition is to take place—especially with a stable explosive. A test at a comparatively low temperature (as 70°), although too high to imitate actual conditions of the powder during storage, approaches more nearly to these conditions than tests at 115° or 135°.

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[1] Mitth. Gegenst. d. Artill. Geniewesens, 1879, 345; Dingl. Poly. 1879, **234**, 43; abst. Wag. Jahr. 1879, **25**, 398; Zts. Chem. Grossgewerbe. 1879, **4**, 287; Chem. Ztg. 1879, **3**, 688; Chem. Tech. Rep. 1879, **18**, I, 286; Chem. Centr. 1880, **51**, 192.

In G. Patterson's surveillance test[2] for smokeless powders, 10–15 gm. of the powder are heated in a glass vessel which is especially resistant to the action of nitrogen oxides. For the largest size powders heated at 65.5° a period of 300–400 days passes before brown fumes appear—if the powder is stable. At 80° brown fumes appear in about 100 days. For old powders the above periods are less dependent on the stability of the powder.

The Waltham Abbey silver vessel test (which is suitable for certain types of cordite and for gelatinized powders containing a high nitroglycerol content) is carried out as follows:

The sample is ground as fine as for the heat test, from 40–50 gm. being placed in a glass vessel surrounded with a vacuum jacket, silvered in order to minimize the loss of heat. A long tube is fused in the neck of the vessel and at right angles to it, in order to better observe the appearance of any red fumes as soon as liberated, a thermometer passing through the neck and being imbedded in the sample of powder. The vessels are placed in a thermostat at 80°, ±0.1°. After some time red fumes are observed in the side tube, the temperature of the cordite begins to rise as indicated by the thermometer imbedded in it, the time being noted for the first rise of 2°. When first manufactured, a satisfactory cordite will stand this test from 500 to 600 hours, the explosive being considered unserviceable, and is destroyed, when the test falls below 200 hours.[3,4]

[1] Ann. Rept. H. M. Insp. Expl. 1905, 28.

[2] Seventh Inter. Cong. Appl. Chem. 1909. Zts. Schiess. Spreng. 1910, **5**, 47; abst. Chem. Zentr. 1910, **81**, I, 1650; Jahr. Chem. 1910, **63**, 426; Wag. Jahr. 1910, **46**, I, 499.

[3] Complete directions for performing this test may be found in "Reg-

In the test of J. Simon-Thomas[1] a higher temperature than that required for the above tests is employed and the experiment carried out over eight days. The explosive is placed in the bottom of a carefully cleaned cylinder (16 cm. high, 1.5 cm. diam.) fitted with a ground-glass stopper. It is heated in an oil bath at a particular temperature (90°, 95° or 100°) for eight hours a day, and left in the oil-bath over night, the heating being continued until the appearance of red fumes are observed. The test is carried out in duplicate. Satisfactory powders containing nitroglycerol should stand four days' heating at 95° and an ordinary nitrocellulose powder should stand for three days (i. e., 24 hours' heating) at a temperature of 100°. At 95° stable guncotton will stand over 20 days' (160 hours) at 95° without showing brown fumes.

The Vieille test is more drastic than the Abel test. It can, however, be regarded only as a preliminary test, as it is not strictly quantitative. 10 grams of the explosive is heated at 110° in a strong glass tube or bottle in a specially designed bath, a piece of standard blue litmus paper being placed above the sample and the tube closed air-tight. Heating is continued in the air-bath until the litmus paper is entirely reddened. The time required for the reddening is noted, after which the tube is removed and opened. This test is continued each day, until the time required to redden the litmus to the standard tint is not over an hour, a clean tube and fresh paper, of course, being used each day. The daily times are added and the total accumulated time should not be less than thirty hours for powders for 5 in. and larger guns, twenty hours for powders designed for less than 5 in. guns, and ten hours for nitrocellulose.[2] This test has been

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ulations for Army Ordnance Service," Wyman & Sons, Publishers, 1908, II, 162–167.

4. On account of the large volume of explosive operated upon, it is discreet to carry out the test in a special building removed from other structures. The temperature of the bath may be kept constant by boiling a mixture of water and methylated spirit, or benzene, or by means of a regulator such as the Lowry.

[1] Zts. ang. Chem. 1898, **11**, 55, 1003, 1027; abst. Wag. Jahr. 1898, **44**, 382; J. S. C. I. 1898, **17**, 1179, 1180; 1899, **18**, 174; Chem. Centr. 1899, **70**, I, 76, 509; Jahr. Chem. 1898, **51**, 1879; Meyer Jahr. Chem. 1898, **8**, 327.

[2] On account of the volatility of nitroglycerol and its danger of explosion, blasting gelatin and similar nitroglycerol-containing explosives cannot be tested by this method. For "Optical Indicator of the Decomposition of Smokeless Powders," see J. Bouchaud-Praceiq, F. P. 413821, 1909; also

adopted officially in France, and in some other countries, but the results obtained by this test have been regarded by Sy[1] and some others as unreliable.[2]

According to A. Sy, the test shows solely the acids produced in the decomposition. It is difficult to obtain uniform conditions in the experiment owing to the necessity in obtaining equal pressures in all the bottles, and also to the need for the employment of litmus of uniform grade. The litmus indicator is much less sensitive than the test paper of Abel or of Guttmann.

The litmus paper in the above test may be replaced by methyl violet paper. However, unless the latter is produced under carefully standardized conditions, the results obtained will be unreliable. The method of preparing the paper is as follows: A small quantity of the dipping solution (about 100 cc.)[3] is placed in the deep angle of an inclined "deep-form" rectangular glass tray and a "quarter" sheet is dipped as a unit. In dipping, the strip[4] is suspended from both ends, drooping, so that the first end dips into the solution to within a quarter of an inch of the edge, then the paper is slowly drawn up the side of the dish, drawing the remainder of the strip through the solution. Taking the strip through the solution should occupy thirty seconds; drawing the strip up the sides of the glass dish removes surplus solution. The strip should then be held horizontally and gently waved to and fro so as to preclude the possibility of the solution collecting in spots. The alcohol rapidly dries so that within a minute the strip may be suspended vertically without danger of the solution running. When air-dry, the paper is ready to be cut to the regular size of 30 x 70 mm. for use in the German test. 100 cc. of solution makes about 250 of those strips. The so-called

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J. S. C. I. 1908, **27**, 961; 1909, **28**, 1007, 1105. For determination of relative amounts of smoke produced from smokeless powders, see H. Rebenstorff, Zts. Schiess. Spreng. 1908, **3**, 45.

[1] J. A. C. S. 1903, **25**, 555; J. Frank. Inst. 1908, **166**, 249, 321, 433. He finds the results are reliable only when the explosive is either very good or bad.

[2] As the reddening of the litmus indicates the presence only of acid products, it is affected by the moisture content of the sample. The papers used by the U. S. Ordnance Department are the same as described under the "135° test."

[3] The dipping solution consists of 0.25 gm. pure basic rosaniline (converted to acetate); 0.168 gm. methyl violet (crystals); 4 cc. pure glycerol and 30 cc. water.

[4] The strip is made from Schleicher and Schuell filter paper No. 597.

Ordnance Department test at 115° was devized by A. Sy.[1] This simple test, which it is claimed is not subject to the variations found in many stability determinations, is carried out as follows: From 1 to 4 gm. of nitrocellulose are heated in a watch glass in a thermostat kept at 115°. The watch glass and powder, after eight hours of heating are cooled in a desiccator and weighed. The process is repeated daily for six days or less. In this test it is claimed that the powder is heated in its natural condition and all the products of decomposition are taken into consideration and not merely the acids or nitrogenous products. The test also affords, so it is claimed, an indication of the effect of small quan-

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[1] J. A. C. S. 1903, **25**, 549; abst. J. C. S. 1903, **84**, ii, 617; J. S. C. I. 1903, **22**, 511, 924; Jahr. Chem. 1903, **56**, 1018; Arms and Expl. 1903, **11**, 120; Chem. Centr. 1903, **74**, I, 1056. See also J. Frank. Inst. 1903, **155**, 161; abst. J. S. C. I. 1903, **22**, 511; J. U. S. Artil. Sept-Oct., 1903. According to A. Sy, the Abel test is too much influenced by various conditions to be considered reliable. The zinc-iodide starch modification is more sensitive than the Abel test, and has all the weak points of the latter. Guttmann's diphenylamine test (J. S. C. I. 1897, 283–290) is stated to give unsatisfactory results. Hoitsema's test (J. S. C. I. 1899, 857) is too sensitive, and the reaction may be masked. The explosion test, which consists in gradually heating 0.1 gm. of the sample in a strong test tube on a oil-bath until explosion occurs, can only be regarded as a rough guide to stability, but is of some value in conjunction with other tests. The J. Thomas test (J. S. C. I. 1898, 2280) is stated by H. Aspinwall (J. S. C. I. 1902, 687) to be open to the objection that the length of time required to obtain definite results is too great. The 135°, or German test, is regarded by the author as one of the best of the stability tests. The Vieille test (J. S. C. I. 1902, 688) suffers from the defects. (1) Only acid products of decomposition are shown. (2) It is practically impossible to get all the Vieille bottles equally tightly closed, and consequently the pressure varies in different experiments. (3) Varying results are obtained, unless the litmus papers be uniform. The Will test (J. S. C. I. 1901, 609–617; 1902, 1470, 1554, 1555) gives unsatisfactory results, the defective features being as follows: (1) The temperature of 135° C. is too high for stability testing purposes. (2) The decomposition is measured only by the nitrogen evolved. (3) It is not very clear where the line is to be drawn between a stable and an unstable product. (4) Since in the test the amount of unchanged material is constantly decreasing, it does not seem probable that, even with perfect product, equal amounts of nitrogen would be evolved in equal intervals of time. (5) It is practically impossible to get carbon dioxide free from air, and as it is exceedingly difficult to pass the gas through the apparatus at a uniform rate, its air-content gives rise to serious errors. If the carbon dioxide be passed too quickly, it is not sufficiently heated in the preheating coil before it comes in contact with the sample, and it also may not be completely absorbed by the caustic soda; if it be passed too slowly, the gases of decomposition are not carried away fast enough, and this may affect the course of the decomposition. (6) Quite unstable products are liable to explode.

At the Frankford Arsenal all nitrocelluloses and nitrocellulose powders are examined by the Abel test, the explosion test, the 135° C. test, and the Vieille test, and it is stated that a careful application of these four tests allows of the detection of an unstable product.

TABLE CLI.—NITROCELLULOSE (12.35% N) FOR MILITARY POWDER

Purification.—Boiled, before pulping, three times for 12 hours, in slightly acid water. Then six times for three hours. Each washing with hot water is followed by washing with cold water

Temperature 140° C.

Weighings after Two Hours Heating	Loss in Mgm. per Gm. of Nitrocellulose				
	Standard Nitro-cellulose	Pulping and One Washing	Fine Pulping and Three Washings	Four Extra Washings	Addition of $HgCl_2$ $\frac{1}{10,000}$
1	5	10	8	7	9
2	4	9	7	6	7
3	4	8	7	6	6
4	6	10	8	7	8
5	5	12	9	7	7
6	7	14	8	8	9
7	7	17	10	8	8
8	7	17	12	9	9
9	9	17	12	9	10
10	9	17	12	9	10
11	11	17	12	11	11
12	10	17	12	11	11
13	11	17	12	12	13
14	13	17	12	15	14
Manometer test (Obermüller) test 140° C. (mm. of Hg)	6	12	8	7	9
	6	18	9	7	8½
	8	26	10½	9	8½
	9	29	11½	10	11
	11	34	13	12	11
	11	..	..	12	13
	12	..	..	13½	13
	13	.	..	15	14
Abel test, 80° C.	31 min.	4 min.	8 min.	18 min.	over 1 hr.
Vieille test, 110° C.	22 hrs.	7 hrs.	11 hrs.	13 hrs.	15½ hrs.
Light brown fumes, 135° C.	48 min.	19 min.	26 min.	39 min.	33 min.

tities of added substances or foreign matter on the stability. The long time (1 week) required for the carrying out of this test militates against its general use.[1] In the modified test of M. Jacqué a shorter time is required. The nitrocellulose is heated to constant weight at 50°–60 and afterwards for 10 minutes at 130° to drive off the last traces of moisture, then desiccated and finally weighed. The dry sample is kept for two hours at a tem-

[1] R. Escales, Zts. angi Chem. 1905, **18**, 940; abst. Wag. Jahr. 1905, **51**, I, 458; Jahr. Chem. 1903–1908, II, 976; Chem. Centr. 1905, **76**, II, 281. See also Wag. Jahr. 1905, **51**, I, 458.

perature of 1[illegible]0–140°, cooled in vacuo over sulfuric acid and the loss in weight rapidly determined on a Curie balance. This process is repeated fifteen times. The results are calculated on the basis of the loss in mgm. per gram of nitrocellulose taken. The samples are usually heated with free excess of air, although the experiment may be modified so that the reaction takes place with the products of decomposition present. In this case the glass weighing vessel is enclosed in a second vessel which is provided with a close-fitting air-tight cover. The above table compares a typical analysis by M. Jacqué's method with the results obtained in the tests of Obermuller, Abel, Vieille and the 135° fume tests, of a nitrocellulose under different conditions.[1]

A compact apparatus suitable for the heating of explosives at constant temperature has been described by J. Brame,[2] consisting of three parts: (1) the boiling and heating jacket, (2) the decomposition and measuring apparatus, and (3) a mercury pump. Constant temperature is secured by utilizing the vapor from a liquid of constant temperature to heat the apparatus.[3,4] For the experiment at 110° toluene is employed, at 115° a mixture of toluene (3 vols.) and xylene (1 vol.) and at 130°, amyl alcohol is used (see Fig. 289).[5]

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[1] Zts. Schiess. Spreng. 1906, **1**, 395; abst. J. S. C. I. 1906, **25**, 1117.

[2] Zts. Schiess. Spreng. 1912, **7**, 216; C. A. 1912, **6**, 1229; 1913, **7**, 257; J. S. C. I. 1912, **31**, 159, J. C. S. 1912, **102**, ii, 394.

[3] W. Hodgkinson and A. Coote, Chem. News, 1905, **91**, 494; abst. J. C. S. 1905, **88**, ii, 488; J. S. C. I. 1905, **24**, 560; Bull. Soc. Chim. 1906, **36**, 143; Chem. Centr. 1905, **76**, I, 1522.

[4] "Service Explosives, 1907."

[5] A. Mittasch, Zts. ang. Chem. 1903, **16**, 929; abst. Chem. Centr. 1903, **74**, II, 926; J. S. C. I. 1903, **22**, 1208; Jahr. Chem. 1903, **56**, 1018; Meyer Jahr. Chem. 1903, **13**, 345; Wag. Jahr. 1904, **50**, I, 357.

In his method, the decomposition vessel consisted of a small tube of about 8 cc. capacity, provided, by means of a ground-glass connection, with an outlet tube for the gases. This was heated in a thermostat, which consisted of a small closed vessel, filled with aniline and connected, by a side tube, with a gas regulator; the thermostat was formed with a deep central indentation, forming an air-bath, in which was placed the decomposition vessel. The gases evolved passed to a U-tube filled with paraffin oil; in the narrower limb of the U-tube was a glass float, connected by means of a long piece of narrow glass tubing with a glass pen filled with ink. The pressure of the gas forced the float upward, and the movement was recorded, by means of the glass pen, upon a sheet of cardboard, to which a uniform horizontal movement was imparted by a clockwork arrangement. The experiments with nitro-cellulose were carried out at 140°. About 0.12 gm. of the sample was well mixed with a diluting agent (sea sand, quartz powder, powdered marble, kieselguhr) and introduced into the carefully cleaned and dried decomposition vessel. Complete decomposition of the nitrocellu-

Will's Stability Test.[1] A 2.5 gm. sample of cellulose nitrate is packed in a decomposition tube 15 mm. wide and 10 cm. high, and heated by an oil bath to 135°, the oxides produced by decomposition of the nitrate being passed over ignited copper, where they are reduced and the nitrogen retained in the measuring tubes.[2]

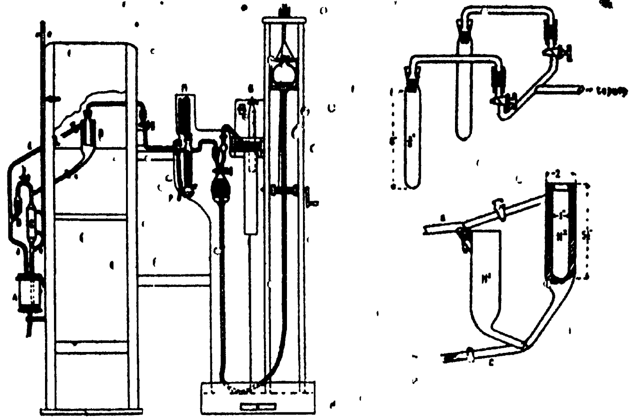

FIG. 289.—THE BRAME CONSTANT TEMPERATURE HEATING APPARATUS FOR EXPLOSIVES

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lose was effected in about one day. The slow decomposition of nitrocellulose is a process which is catalytically accelerated by the products of the reaction. With the same sample, the velocity of decomposition varies considerably with the cleanness of the decomposition vessel and the nature and proportion of the diluting material. The best diluting material was found to be sea sand well purified by boiling with acid and subsequent strong ignition. The addition of substances of a distinctly basic character retarded the decomposition, but decomposable nitrogenous compounds, e. g., ammonium nitrate and urea, considerably accelerated it.

[1] W. Will, Mitt. a. d. Centrahlstelle f. Wissench. Tech. Unters. Nuo-Babelsberg, 1902, (2), 5; J. S. C. I. 1901, **20**, 609, 932; 1902, **21**, 1490, 1554; Z. ang. Chem. 1901, **14**, 743; Chem. Centr. 1901, **72**, II, 606, 667; Jahr. Chem. 1901, **54**, 894; Meyer Jahr. Chem. 1901, **11**, 316; Tech. Chem. Jahr. 1901, **24**, 204; Wag. Jahr. 1901, **47**, I, 501. Also Kismiensky, Mem. des Poudres Salpêtres, 1905-1906, **13**, 247; abst. J. S. C. I. 1907, **26**, 892.

[2] The principle of this test depends upon the regularity with which a cellulose nitrate is decomposed under conditions which permit of the removal and estimation of the products of decomposition, especially the nitrogen. The temperature of 135° is employed, the ester being kept in a constantly changing atmosphere of carbon dioxide, heated to the same temperature. The oxides of nitrogen formed are passed over red-hot copper, where they are reduced to nitrogen, and finally the rate of evolution of nitrogen is measured. According to Will, the best criterion of a stable cellulose nitrate

The air in the apparatus (Fig. 290) is first entirely displaced by a stream of CO_2 from a generator[1] or gas holder, the gas being purified by passing through scrubbers. The stream of gas is maintained during the whole of the operation, being absorbed at the end of the system by solution in KOH.[2] The pressure and rate of flow of gas must be very carefully measured, and this is arrived at by counting with a stop-watch the number of bubbles of gas per minute which bubble through an interposed wash bottle of sulfuric acid.[3] The preheating worm in connection with the decomposition tube is of the thinnest hydrometer stem tubing,

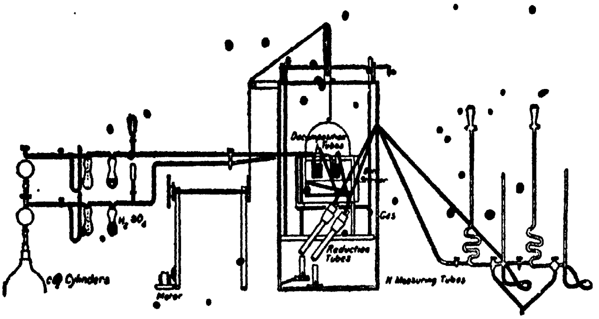

FIG. 290.—WILL'S APPARATUS FOR TESTING NITROCELLULOSE AS MODIFIED BY ROBERTSON

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is that it shall evolve at high temperatures equal quantities of nitrogen in equal periods of time. For the accuracy of this test, it is essential that the material should be purified to the limit, so that continued washing produces no further speed in decomposition when tested by his method.

[1] Objection has been raised to the use of compressed CO_2 in steel cylinders from the danger of the presence of varying amounts of air present, the nitrogen present in which would lead to fictitious results. It has been found, however, that it is quite possible to produce this gas commercially with as little as 0.01% air present—an entirely negligible quantity. Estimations of air present in a cylinder of this gas show that even when the CO_2 is nearly exhausted the residual gas contains but a very small amount of air, insufficient to influence the accuracy of the determination. A micrometer screw attached to the main valve of the cylinder is useful for governing the rate of flow of gas. A blank experiment is usually made to determine the amount of air in the CO_2, and correction made in the final readings.

[2] To guard against the possibility of explosion, the decomposition tube and oil bath are encased in strong iron and glass walls.

[3] A mercury manometer is connected here and is useful in detecting possible leaks in the apparatus. If the flow of gas be too rapid, it does not become sufficiently preheated in the glass spiral, and if too slow there is too rapid decomposition of the ester by the nitrogen oxides evolved, which are not removed.

the ground-in exit tube being kept in position by a small screw clamp with trunnion bearings.

The reduction tube in which the oxides of nitrogen are reduced to nitrogen is made of copper and consists of two parts, an outer tube and an inner tube leading nearly to the bottom of the former. In the inner tube fits a spiral of reduced copper gauze and the annular space between the tubes is filled a lightly packed, reduced copper spiral. At the bottom, the inlet tube dips into a layer of copper oxide asbestos, on the top of which is a layer of reduced copper asbestos. Through the India rubber stopper passes a glass tube, which leads the carbon dioxide and nitrogen out of the reduction tube. As the portion of the tube containing the spirals is heated to redness, water jackets are provided on both inner and outer tubes to protect the India rubber cork. This reduction tube may very conveniently be replaced by a small combustion tube filled with copper and copper oxide in a somewhat similar manner as for a nitrogen determination in an organic compound.

To permit of duplicate experiments being made at the same time, the bath is adapted for two decomposition tubes. The bath itself is filled with high-flashing lubricating oil and fitted by/with a lid with two circular openings for the spiral tubes. This is surrounded by an asbestos-covered envelope, in the interior of which circulate the products of combustion of the numerous gas jets used.[1] A nitrogen-measuring apparatus with zigzag tube is used, having been found more economical in potash.[2] The results are best expressed by plotting on coördinate paper, letting the time in hours and the milligrams of nitrogen be the two factors. When the speed of carbon dioxide is about 1,000 cc. per hour, a line of nitrogen evolution is obtained which is curved and forms a satisfactory representation of the inherent instability of the material.[3]

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[1] The stirrer, operated by a water motor, or electrically, has a series of helical blades, curved to thoroughly mix the oil. By this means a great constancy of temperature is maintained. The bath should also be equipped with a temperature regulator and delicate thermometer.

[2] The readings may be more conveniently taken by counterbalancing the column of potash solution and reading off the volume of gas at atmospheric pressure. To do this, momentarily close the tap directly in front of the measuring tube, which does not interfere with the progress of the test. The air correction is subtracted from each reading, and the remainder brought to the weight of nitrogen by the usual methods of calculation.

[3] Will recommends a speed of 1,500 cc. per hour, but it has been found that when the evolution of gas is slower, slight differences become more

The steepness of the curve formed by thus plotting the results is an indication of the stability of the ester under examination. The sharper or more abrupt the curve, the more nitrogen is evolved in a given unit of time, and the lower the stability.[1]

2.5 grams of a stable nitrocellulose (N = 13%), when tested according to the Robertson modification, will evolve from 4–6.5 mgm. of nitrogen in four hours. The above test has mainly proved its success in connection with the testing of ungelatinized nitrocellulose. It has, however, been used to a limited extent for gelatinized nitrocellulose. It is not generally suitable for gelatinized powders containing stabilizers or nitroglycerol.[2]

In connection with gelatinized explosives, the following experiments by R. Robertson[3] are of interest. The nitrocellulose powder was ground in a mill, passed through a 100-mesh sieve, and 2.5 grams used for a Will test. The test was carried out for eight hours, for the purpose of ensuring that there was no delay in the evolution of nitrogen owing to the gelatinized form of these explosives, even when the substance was in a fine state of division. (A) is a good nitrocellulose powder according to all tests, (B) is one on which heating has passed through a stage of instability, as a result of which it has a diminished Abel test. (See Fig. 291.)

It has also been proposed[4] to modify the test so that the

apparent, and relationships are evident which would be obscured by the greater gas evolution.

[1] Several hours are required to completely eliminate the air from the apparatus. The fifteen minutes stated by Will has been found insufficient. Readings are commenced thirty minutes from the commencement of heating the cellulose nitrate, and are continued at fifteen-minute intervals for a further period of four hours. Fresh caustic potash solution is added every half hour or so. When unstable esters are heated under the conditions of this experiment, the separation of nitrogen is much greater at the commencement of the operation than later. If the product be very unstable, explosion is liable to ensue. A cellulose nitrate is regarded as "normal" (satisfactory) when the nitrogen separation is uniform throughout the process. If the absolute amount of nitrogen separated is to be determined, the ester must be accurately weighed; the air in the CO_2 carefully estimated, and the reduction of all gas volumes to 0° and 760 mm. pressure be made. See also G. W. Patterson, "Stability Tests of Smokeless Powders," Seventh Int. Cong. Appl. Chem., London, 1909.

[2] R. Robertson and S. Napper, J. C. S. 1907, **91**, 761, 764; abst. C. A. 1907, **1**, 1772; J. S. C. I. 1907, **26**, 638; Chem. Zentr. 1907, **78**, II, 95; Wag. Jahr. 1907, **53**, I, 438.

[3] R. Robertson, J. S. C. I. 1902, **21**, 819; abst. Mon. Sci. 1903, **59**, 658; Chem. Centr. 1902, **73**, II, 540; Jahr. Chem. 1902, **55**, 1055.

[4] Riess, J. S. C. I. 1902, **21**, 680. See also H. Aspinwall, J. S. C. I.

decomposition is carried out at 135° in vacuo instead of a current of carbon dioxide.

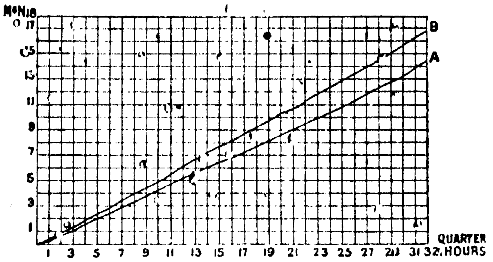


FIG. 291.—NITROCELLULOSE POWDERS—EIGHT-HOUR TEST

A. Baschieri modifies[1] the Will test by removing the decomposition products in a current of air, free from carbon dioxide, and conveying into 0.01 *N* alkali solution. The amount of acid products absorbed after a given time are determined. Stable nitrocellulose, it is claimed, does not cause a saturation of more than 2.5 cc. of the alkaline liquor in two hours; this is equivalent to 0.00035 gram of nitrogen. Lower nitrated nitrocelluloses when thoroughly stabilized give slightly lower results than the above.

The Bergmann and Junk Test. The stability test of W.

1902, **21,** 687; abst. Chem. Centr. 1902, **73,** II, 167; Jahr. Chem. 1902, **55,** 1055.

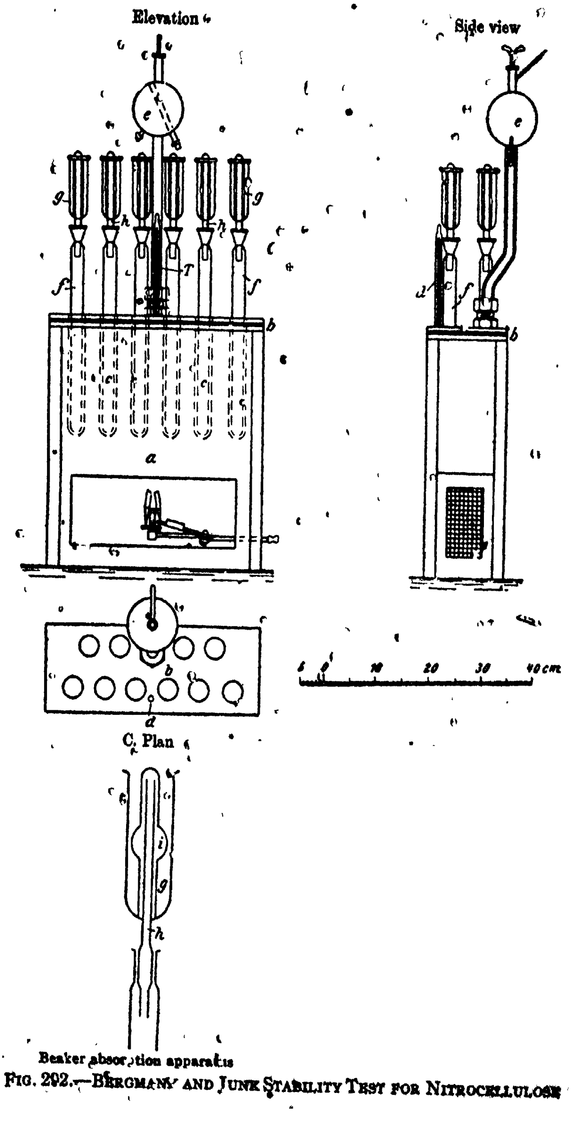
[1] II Nat. Cong. Appl. Chem. Turin, 1911; Zts. Schiess Spreng. 1912, **7,** 41; abst. C. A. 1912, **6,** 1226 J. S. C. I. 1912, **31,** 204; Chem. Zentr. 1912, **83,** I, 1264; Meyer Jahr. Chem. 1912, **22,** 334. His process comprized (1) Separation of the mixed acid, (2) two washings in cold water containing 0.05% sulfuric acid; (3) two hours' boiling in water of the same acidity; (4) two washings in cold water; (5) two hours' boiling in water containing 0.1% sodium carbonate; (6) two washings in cold water; (7) pulping and final washings. As in Robertson's process, the boiling in acid water saponifies the unstable sulfuric or nitrosulfuric esters, but does not affect the more stable nitric esters, the N content diminishing but slightly. The sulfuric compounds are stable at 70° but readily decomposed at temperatures above 100°, and resist alkaline saponification. The latter treatment causes a reduction of 0.2%–0.3% N, due to the breaking up of unstable nitrates of cellulose or hydrocellulose. The stability of the nitrocellulose was determined by means of the Spica modification of the Abel test at 70°, and a modification of the Will test at 135°, devized by Baschieri. In the latter test, 1 gm. of the sample is heated at 135° in a glass U-tube by means of an oil bath with a thermostat. The decomposition products, NO and N_2O_4, are conveyed by means of a current of air free from CO_2 into 0.01 *N* NaOH solution, the saturation of which is determined after a given period of time. Stable nitrocelluloses should not cause a saturation of more than 2.5 cc. in 2 hours, corresponding to 0.00035 gm. Baschieri's process gave a product with a test of less than 2 cc., and Abel test 35 minutes.

Will shows a marked advance in the method of judging the stability of explosives. The high temperature in the decomposition of the nitrocellulose and also in the rate of evolution of oxide of nitrogen over a definite period are valuable determinations from which to arrive at conclusions with regard to the stability of the material under examination. The "Will test," however, is somewhat elaborate and for general works practice, or where an extensive number of qualitative stability estimations are required, a simpler and yet reliable test with a quantitative basis is needed. The best test in the author's opinion to replace the Will test for works practice, is the tests devized by E. Bergmann and A. Junk.[1] This test, which agrees well with that of the "Will," is, in reality, a development along quantitative lines of the so-called German test at 135°. The personal errors in this latter and the errors due to variations in paper, etc., are avoided in E. Bergmann and A. Junk's test and instead, an accurate measurement is secured of the decomposition of the nitrocellulose when heated under standard conditions. The test is carried out at 132°, while as we have already seen, the W. Will and the German tests are carried out at 135°. It is claimed that 135° is too near the critical temperature for the former test to be carried out at 135°. The experimental evidence in favor of using slightly different temperatures in the estimation, however, is small, and a gain would be made in uniformity of testing, if a single temperature were selected for all the tests.

This substitute for the W. Will test is suitable for the examination of ungelatinized nitrocellulose. In its original form as devized by E. Bergmann and A. Junk it is unsuitable for either gelatinized nitrocellulose or for nitroglycerol. Mercuric chloride or dry calcium carbonate show practically no influence on the rate of decomposition of nitrocelluloses in the test. It is influenced, however, by the presence of urea[2] and various stabilizers. It is claimed that the test does not distinguish so sharply as the heat test between the various stages of washing of nitrocellulose. Again, according to Dupré, tests made on the same sample give

[1] Zts. ang. Chem. 1904, **17**, 982, 1018, 1074; abst. J. S. C. I. 1904, **23**, 953; Chem. Centr. 1904, **75**, II, 746; Jahr. Chem. 1904, **59**, 1197; Mon. Sci. 1906, **64**, 45; Chem. Centr. 1904, **75**, II, 746; Meyer Jahr. Chem. 1904, **14**, 369; Tech. Chem. Jahr. 1904, **27**, 194; Wag. Jahr. 1904, **50**, 358; J. C. S. 1904, **86**, ii, 687.

[2] Dupre, Ann. Rep. H. M. Ins. Exp. 1904, 28; 1905, 28.



Beaker absorption apparatus

FIG. 292.—BERGMANN AND JUNK STABILITY TEST FOR NITROCELLULOSE

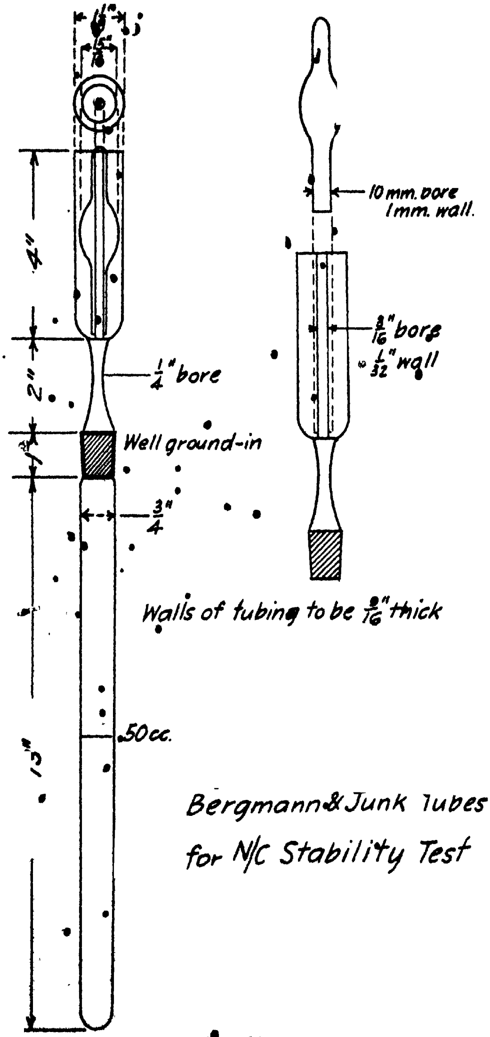
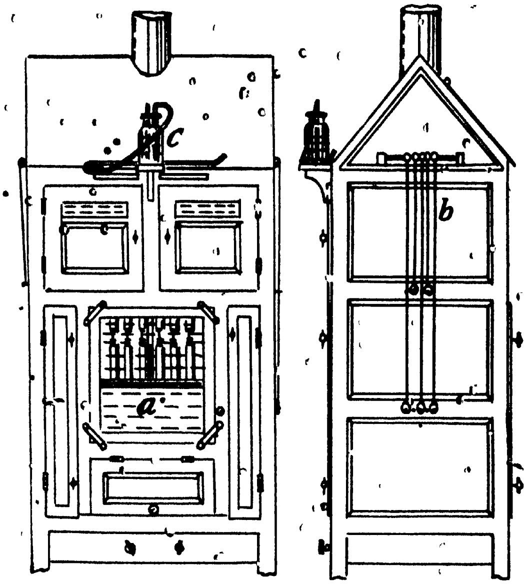

1"
5/16"
4"
2"
1/4" bore
1"
Well ground-in
3/4"
Walls of tubing to be 1/16" thick
13"
50cc.
10mm. bore
1mm. wall.
3/16" bore
1/32" wall
Bergmann & Junk Tubes
for N/C Stability Test

FIG. 293

occasionally widely different results, due, it is suggested, to the fact that the products of decomposition are left in contact with the sample throughout the test, whereby very small differences in the rate of decomposition at the beginning of the experiment



Front view Side view

FIG. 294.—HOUSING FOR BERGMANN AND JUNK STABILITY APPARATUS.

(It is recommended to enclose the apparatus in a housing as shown, in the front and rear of which double sheets of glass, *a*, separated by rubber bands and 8–9 mm. thick, are inserted. A large vent pipe connects with a flue. As shown in the side view, each small tube is connected by means of a string and pulley, so that it can be pulled up out of the apparatus without necessitating the disturbance of others, or opening up the housing. As shown at *c*, the small funnels on the spherical addition, can be filled with water from the outside.)

would be greatly aggravated at the end. The author (Worden) has supervized the working of thousands of Bergmann and Junk tests in duplicate on purified 13.0% N guncotton. When care is taken in the carrying out of the test the results of duplicate tests show a remarkable agreement in practically every estimation. Moreover, "Will" tests were also carried out on about

10% of the guncotton, and there was a very close agreement between the two tests.

In the Bergmann and Junk test, which was adopted by the Prussian military authorities as early as 1900, the nitrocellulose is heated in a glass tube at 132° and the oxides of nitrogen absorbed in water and estimations made at the end of the reaction by the Schultz-Tiemann method. The latter may be employed as follows: One-half of the filtrate from the heated nitrocellulose (25 cc.), equivalent to one gram of nitrocellulose, is placed in a decomposition vessel (Jena flask, 300 cc.), and boiled until all air is expelled from the apparatus through an outlet. The flask is then allowed to cool slightly and 15 cc. each of ferrous chloride and hydrochloric acid are drawn into it by suction through a small thistle tube. The nitrocellulose solution may also be run in from a funnel to the iron solution. The flask is then again heated to boiling and the evolved nitric oxide passed into a measuring burette standing in a dish containing water previously boiled, and mercury. A known amount of standard potassium nitrate solution is now placed in the flask and the foregoing operation repeated, the liberated gas being passed into another burette. [10 milligrams of the potassium nitrate will yield 2.21 cc. of dry "NO" at 0° and 760 mm.—the factor for correcting the observed volumes of gas from the unknown solution corrected to standard conditions of temperature and pressure.] This method of analysis is both quick and accurate. Many other methods have also been suggested for estimating the small quantity of nitrogen compounds formed.

The amount of nitrogen (as nitric oxide) liberated in 2 hours from 2 grams of purified nitrocellulose is usually less than 5 cc. of nitric oxide which corresponds to 2.2 cc. of $N/10$ alkali or 3.2 milligrams of nitrogen. Direct titration is open to the objection that a small error makes an appreciable alteration in the result. The evolved nitrogen compounds might be converted into nitrate and the nitrate estimated by phenolsulfonic acid or by reduction to ammonia, but the Schultz-Tiemann method is to be preferred. The heating bath is a rectangular copper vessel 35 x 10 cm. and 25 cm. high, containing 10 tubes each 20 cm. long let into it to take the glass tubes. The boiling is carried out in heavy, thick-walled tubes 35 cm. long and 2 cm. internal diameter, a hollow glass stopper surmounted by an absorption apparatus being ground into the neck. The heating bath carries a bath to indicate the temperature, *iso*amyl alcohol[1,2,3,4] or other suitable liquid being used in maintaining the constant temperature. The guncotton is first dried at 50° in a good current of air for 1 hour, then sieved and finally dried 5 hours at 80°. It is sometimes recommended to finish the drying in a desiccator over sulfuric acid until the sample contains not over 1% moisture. In laboratory practice it is more convenient and leads to greater uniformity by the adoption of the former practice. It is necessary to emphasize the importance of a fixed moisture content as the presence of moisture

[1] H. Caron (Ann. Chim. Analyt. 1911, **16**, 211; abst. J. S. C. I. 1911, **30**, 837; J. C. S. 1911, **100**, ii, 767; C. A. 1911, **5**, 2792; Chem. Zentr. 1911, **82**, II, 390. See also Bull. Soc. Chim. 1910, **7**, 1021, 1025; abst. Chem. Zentr. 1911, **82**, I, 350 finds that the sensitiveness of the diphenylamine test for nitrates depends mainly upon the proportion of diphenylamine and the concentration of sulfuric acid in the reagent and the rise of temperature produced on mixing the solution with the reagent. The best results are obtained with very low concentrations of diphenylamine and high concentrations of sulfuric acid, and the method of carrying out the test recommended is to add 5 cc. of a solution of 2 mgm of diphenylamine in 100 cc. of concentrated sulfuric acid to 2 cc. of the solution under examination. If the solution contains chlorides it is better to use a reagent prepared by dissolving a few mgms. of diphenylamine in a mixture of 100 cc. of sulfuric acid, 40 cc. of water, and 2 or 3 cc. of 10% hydrochloric acid; 5 cc. of reagent are added to 0.5 cc. of the solution to be tested. The reaction may be masked by organic substances such as methyl and ethyl alcohols, glycerol, ether, acetone, hydrocarbons, salicylic acid (J. S. C. I. 1911, 711), and phenol, especially when the solution of diphenylamine in concentrated sulfuric acid is used, and it is, therefore, better to use the dilute reagent containing hydrochloric acid, mentioned above, when organic matter is present.

[2] Bull. 107, Div. Chem. U. S. Dept. Agri.

[3] W. Withers and B. Ray, J. A. C. S. 1911, **33**, 708; abst. J. S. C. I. 1911, **30**, 708; C. A. 1911, **5**, 2045; J. C. S. 1911, **100**, ii, 656; Chem. Zentr. 1911, **82**, II, 489. The reagent is prepared by dissolving 700 mgm. of diphenylamine in a mixture of 60 cc. of concentrated sulfuric acid and 28.8 cc. of distilled water, cooling the solution and then adding slowly 11.3 cc. of hydrochloric acid of sp. gr. 1.19. After standing over night some of the diphenylamine should separate, showing that the solution is saturated. In making a test, 1 cc. of the liquid under examination is mixed thoroughly with 1 drop of the diphenylamine reagent, and then 2 cc. of concentrated sulfuric acid are added from a pipette, so that two layers are formed. The whole is agitated gently so as to cause a slight mixing of the liquids at the plane of contact, and then kept at 40° C. for 15 or 20 minutes. It is stated that in this way 1 part of nitrite nitrogen in 25 millions or 1 part of nitrate nitrogen in 35 millions can be detected, while, by heating at 40° C. for 1 hour, the delicacy is increased to 1 part in 32 millions or 1 part in 44 millions, respectively.

[4] A small iron casing which need not be closed on top is, however, more suitable. It should be fitted with a sliding door and contain a small window fitted with duplex glass. The cupboard for preference should be fixed opposite a window (also having duplex glass) so that evolution of fume could readily be seen in Bergmann and Junk tubes.

has a definite influence on the decomposition, which increases appreciably with increased water content. According to Dupré, in the case of samples of nitrocellulose which were not perfectly purified, the presence of water, especially influenced the result. He insists on the limits of moisture in the sample under test being rigidly observed. About 2 gm. are weighed out, introduced into the apparatus, any adhering particles being brushed down with a feather or camelshair brush. The glass stopper is then inserted, the beaker half-filled with water, the glass tube being introduced into one of the holes in the bath, the temperature of the latter being at 132°. Heating is continued for two hours, after which the tube is removed from the bath. As the tube cools and the air contracts, water is drawn from the beaker onto the cotton. The absorption apparatus is washed out into the tube, the volume being made up to the 50 cc. mark indicated on the tube. The liquid is then filtered, an aliquot portion (usually 25 cc.) of the filtrate taken, 1 cc. $N/2$ potassium permanganate solution added to oxidize nitrous to nitric acid, and the nitrogen then estimated as above stated. A satisfactory guncotton should not yield over 2.50 cc. nitric oxide per gm. of original sample in two hours' heating and a stable "collodion cotton" not more than 2 cc.[1]

F. Mayrhofer[2] substituted a 2% solution (20 cc.) of potassium iodide for the water used in the quantitative collection of the decomposition products. In testing the stability of a nitroglycerol powder it is tested both dry and also when moistened with 0.05 gm. of water. A stable powder behaves in a similar manner whether heated dry or moist, whereas an unstable is rapidly decomposed in the presence of a trace of water. By this means variations of stability can be detected which are not apparent in the usual test at 120 degrees.

W. Will[3] has used this modification of the Bergmann and

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[1] It has been noted that heating the guncotton to 132° increases th percentage solubility of the explosive in ether-alcohol.

[2] Zts. Schiess. Spreng. 1918, **13**, 425, 448; abst. Chem. Zentr. 1919 **90**, II, 702; J. S. C. I. 1919, **38**, 603-A; C. A. 1919, **13**, 3320; Ann. Rep. Soc Chem. Ind. 1919, **4**, 542.

[3] Zts. Schiess. Spreng. 1919, **14**, 61; abst. Chem. Ztg. Rep. 191 **43**, 255; abst. J. S. C. I. 1919, **38**, 926-A; Chem. Zentr. 1919, **90**, I, 70 In a previous communication (Zts. Schiess. Spreng. 1918, **13**, 425, 44 abst. C. A. 1919, **14**, 3320) F. Mayrhofer recommends the use of 2 cc. of a 2% KI solution instead of water for the quantitative collecti

Junk test in examining the stability of nitroglycerol powder of various degrees of stability. His results agree with those found by F. Mayrhofer.

The Obermuller Test[1] consists in heating the nitrocellulose in vacuo at a constant temperature (140° C.), and measuring continuously by means of a mercury manometer, the pressure exerted by the evolved gases, the latter being maintained at constant volume. The rate at which the pressure increases is a measure of the rate of decomposition of the nitrocellulose. Pressure tests on a similar principle have been devized by J. Brame[2] and Dupré.[3] The Obermuller apparatus has been improved by B. Pleus[4] so as to give greater facility in operation. The calcium chloride heating bath is replaced by a vapor bath similar to that in use in the Bergmann-Junk test, a mixture of xylol and toluol being used, and the glass tubes immersed in separate brass tubes surrounded by the hot vapors. The manometer is so modified that condensed moisture will not collect over the mercury, but runs directly to a receiver. Four heating tubes with their manometers are connected to one receiver. The rubber connection between the heating tube and manometer is replaced by a ground

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of the decomposition products. For estimating the stability of a diphenylamine containing nitrocellulose colloid, it is tested both dry and moistened with 0.05 gm. of water. A stable powder behaves in the same manner, whether moist or dry, whereas an unstable one is rapidly decomposed in the presence of traces of moisture. By this method, variations in stability can be detected which are not apparent by the usual test at 120°.

[1] P. Obermuller, Ber. Bezirksverein des Ver. Deut. Chem. Oct. 11, 1904; abst. J. S. C. I. 1905, **24**, 347; Jahr. Chem. 1905–1908, II, 978; J. C. S. 1905, **88**, ii, 291; Meyer Jahr. Chem. 1904, **14**, 369; Tech. Chem. Jahr. 1904, **27**, 196; Wag. Jahr. 1905, **51**, I, 452.

[2] Zts. Schiess. Spreng. 1912, **7**, 216; abst. J. S. C. I. 1912, **31**, 159; C. A. 1912, **6**, 1227; J. C. S. 1912, **100**, ii, 394; Chem. Zentr. 1913, **84**, I, 1802.

[3] Ann. Rep. H. M. Ins. Exp. 1903, 26; 1904, 28; 1905, 29.

[4] Zts. Schiess. Spreng. 1910, **5**, 121; abst. Jahr. Chem. 1910, **63**, 424; Chem. Zentr. 1910, **81**, I, 1994. C. A. 1910, **4**, 1806; Meyer Jahr. Chem. 1910, **20**, 328; Wag. Jahr. 1910, **56**, I, 497. The $CaCl_2$ heating bath is replaced by a vapor bath similar to that used in the Bergmann-Junk test, a mixture of xylene and toluene being used, and the glass tubes immersed in separate brass tubes surrounded by the hot vapors. The manometer is so modified that condensed moisture will not collect over the Hg, but runs directly to a receiver. Four heating tubes with their manometers are connected to one receiver, the number of joints required being greatly reduced. The rubber connection between the heating tube and manometer is replaced by a ground glass joint provided with a mercury seal. Detailed illustrations of original and modified apparatus are shown. The new apparatus is obtainable from Bleckmann & Berger, Berlin, N. August Str. 3 a, the bath from E. A. Lenz, Berlin.

glass joint provided with a mercury seal. With the pressure-recording apparatus there is difficulty in preventing moisture from depositing in the tubes leading away from the decomposition vessel. With precaution this trouble may be overcome.[1]

A physical method such as the above, in which direct readings can be obtained, has decided advantage even over a test such as the Bergmann and Junk which involves a certain amount of chemical manipulation. The advantage is all the greater when it is remembered that the pressure-recording test is as reliable as the Will and Bergmann and Junk tests. Unlike this latter test, a series of decomposition stages may be recorded and in this way decomposition curves obtained which will give definite information regarding the progress of decomposition. The apparatus of Obermuller has been used in this connection by O. Wilcox[2] in connection with the examination of various American nitrocelluloses. From the examination of his results it appears that a given sample of nitrocellulose, when heated at 140°, has a characteristic decomposition pressure; as the heating is continued, a new component or phase is produced, which reinforces the previous one by its decomposition pressure; the "pressure-increase" then remains more or less constant until a new phase is again produced, and so the process repeats itself.

An apparatus has been constructed by W. Ostwald[3] which is suitable for recording the increase of gas-volume obtained when nitrocellulose is heated. This type of apparatus has also been used by A. Mittasch[1] for heating nitrocellulose at 150° at the ordinary barometric pressure. A test of a similar nature to that used by A. Mittasch has been employed by Silberrad.[2] The test is carried out at 115° for 20 hours, but instead of measuring change in pressure caused by the evolved gas, the latter is directly collected and measured. According to Dupré[3] the reaction is difficult to control, since even in duplicate experiments widely different results are often recorded. The Ostwald type of apparatus has been used by A. Saposchnikoff and W. Jagellowitsch; the nitrocellulose is heated at different temperatures between 120°–150°.[4] They construct curves by using the volume of gas (v) and the time (t) as ordinates. The curves that have distinct bends show the autocatalytic character of the reactions at these high temperatures. The relation between the temperature and the maximum reaction velocities $\left(\frac{dv}{dt}\right)$ corresponding to the bends in the curves may be represented by two lines, corresponding to the equations:

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[1] R. Robertson and S. Napper, J. C. S. 1907, **91**, 761; abst. C. A. 1907 **1**, 1772; J. S. C. I. 1907, **26**, 638; Chem. Zentr. 1907, **78**, II, 95; Wag. Jahr 1907, **53**, I, 438.

[2] Zts. ang. Chem. 1908, **21**, 1407; J. A. C. S. 1908, **30**, 271; abst. Jahr Chem. 1905–1908, II, 977, 979. Wag. Jahr. 1908, **54**, I, 451; J. S. C. I. 1908 **27**, 246; Chem. Zentr. 1908, **79**, I, 1534, II, 401; Zts. Schiess. Spreng. 1908, **3**, 246.

The samples examined were "decanitrocelluloses" of about 12.60% nitrogen content and 99% solubility in ether-alcohol. The nitrocellulose was heated to 140° C. *in vacuo* and the pressure read off every 15 minutes. During the first four periods the gases were allowed to accumulate and exert pressure; after the first hour the gases were continually withdrawn during the odd periods, and allowed to accumulate during the even periods. Curves showing the relation between time and pressure are then given. For a nitrocellulose of good quality, the author finds that the curve after the end of the first hour ("constant initial pressure") shows a step-like character, being made up of several approximately horizontal portions connected by inclined straight lines.

[3] Zts. phys. Chem. 1900, **35**, 33, 204.

Between 120° and 130°:

$$\frac{dv}{dt}\ \text{max.} = -2.22 + 0.0192t$$

Between 135° and 150°:

$$\frac{dv}{dt}\ \text{max.} = -64.22 + 0.48t$$

These lines intersect at the point corresponding to 135°.

The authors use the term autocatalysis in the sense of a slowly proceeding process which is progressively accelerated by the decomposition products acting catalytically. When nitrocellulose is mixed with certain substances and then heated, interesting changes in the speed and form or nature of the decomposition may be observed. When kieselguhr and nitrocellulose are heated the amount of gas evolved is proportional to the time. With calcium oxide as diluent the volume first decreases but then increases. Magnesium powder, calcium carbonate, oxide of iron or alumina are without influence. Sodium carbonate, copper nitrate and urea exercise a strong increase of the decomposition velocity, connected with a change in the shape of the curves.

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[1] Zts. ang. Chem. 1903, **16**, 929; abst. Jahr. Chem. 1903, **56**, 1018; Meyer Jahr. Chem. 1903, **13**, 345; Chem. Centr. 1903, **74**, II, 926; J. S. C. I. 1903, **22**, 1208.

[2] Treatise on Service Explosives, 1907, 149.

[3] Ann. Rep. H. M. Insp. Exp. 1905, 28.

[4] J. Russ. Phys. Chem. Soc. 1905, **37**, 822; abst. Chem. Centr. 1906, **77**, I, 339; J. S. C. I. 1906, **25**, 191; Meyer Jahr. Chem. 1905, **15**, 358.

Other Stability (Heat) Tests. A modified form of the explosion test has been devized by H. Weber.[1] The proposed method in addition to giving an accurate determination of the explosion-temperature substance gives, it is claimed, a fair comparison of the relative stability of explosive substances. It is applicable, moreover, to gelatinized nitrocellulose and nitrocellulose powders. The test is stated to be a determination of the rate of change of decomposition velocity with change of temperature—and as such—characteristic for each sample. In the test the sample is heated at a constant temperature and the time required to bring about explosion is noted. Temperatures varying between 130°-200° are employed. The bath of paraffin or other material contains several loosely stoppered tubes into which samples of the explosive (whole grains of pieces about 0.2 gm. each), are dropped, the time elapsing before explosion being noted with a stop-watch. The results of the explosion tests at 160°, 170°, 180° and 200° are plotted for each sample. Distinct differences in form are shown by stable and unstable powders, and it is considered that the curves actually represent the stability of the powders with changing temperatures. The requirements of the Ordnance Department for an explosive test may be carried out by the following simple test, which test, however, can only be regarded as an approximate one capable of differentiating between a very good and a very bad powder. A sample of the explosive (usually 0.1-0.2 grams) is placed in a hard glass test tube, tightly stoppered, and placed in a paraffin bath at 100°. The bath is continually stirred and the heat so regulated that the temperature increases 5° per minute. The temperature at which the sample explodes is noted, which is the result sought.[2]

In connection with the uncertainty of testing stability by heating to a comparatively high temperature the following experiments by E. Berl and M. Delpy[1] are of interest. In the course of the purification of nitrocellulose, unstable bodies consisting mainly of nitric esters of disintegrated cellulose material were separated from the nitrocellulose and extracted by alcohol and the alcohol solution evaporated to dryness.[2] The purified nitrocellulose had an ignition temperature of 180.5°, while a mixture containing the pure nitrocellulose with 10%-20% of the unstable products gave an ignition temperature of 180°. This latter mixture undoubtedly consists of an unstable explosive, yet the ignition test did not give indications of this fact.

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[1] Eighth Inter. Cong. Appl. Chem. 1912, 4, 147; J. Ind. Eng. Chem. 1913, 5, 641; Bull. 192 (Reprint) Dept. Comm. and Labor, U. S. Bur. Standards, 1912, 9, Reprint No. 199; C. A. 1913, 7, 2308.

[2] A. Sy (J. A. C. S. 1903, 25, 553) states the standards established by the Ordnance Department for this test to be as follows: A good nitrocellulose should not explode under 186°, that of a nitrocellulose powder under 177°, and a nitroglycerol powder under 170°. Variations in results may be

In a climate trial at comparatively low temperatures, say 40°-60°, an extended period (1 to 3 months) is necessary in order to obtain definite indications regarding the stability of most explosives. It has also been noted by G. Patterson for the detection of sulfuric acid esters that the higher the temperature of the stability test the more easily may such compounds be detected.[3]

The velocity of decomposition of nitrocellulose generally is approximately doubled by a rise of temperature of 5°.[4] For ordinary gelatinized nitrocellulose powders, however, there is probably no test which is as trustworthy and on which conclusions can be as safely based as a prolonged storage test carried out at a comparatively low fixed temperature, 40°-60°, and with periodic examination of the explosive. The possibility of secondary reactions which may occur at high temperature is less

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caused by differences in manipulation of the test, especially in the speed with which the temperature is raised. Greater differences between the explosion points are obtained when the temperature is raised only 1° instead of 5° per minute.

[1] Zts. Schiess. Spreng. 1913, **8**, 129; abst. C. A. 1913, **7**, 2307; J. C. S. 1913, **104**, i, 1305; J. S. C. I. 1913, **32**, 452; Chem. Zentr. 1913, **84**, II, 493; Meyer Jahr. Chem. 1913, **23**, 363; Wag. Jahr 1913, **56**, I, 457; Zts. ang. Chem. 1913, **26**, II, 447. See also W. Cullen, J. S. C. I. 1901, **20**, 8. G. Finzi, Gaz. chim. ital. 1909, **39**, I, 549; abst. J. S. C. I. 1909, **28**, 676. B. Zschokke, Zts. Schiess. Spreng. 1911, **6**, 241.

[2] F. Langenscheidt, Zts. Schiess. Spreng. 1914, **9**, 54; abst. C. A. 1914, **8**, 1669.

[3] Seventh Inter. Cong. Appl. Chem. 1909, Zts. Schiess. Spreng. 1910, **5**, 47; abst. Chem. Zentr. 1910, **81**, I, 1650; Jahr. Chem. 1910, **63**, 426; Wag. Jahr. 1910, **46**, I, 499.

[4] O. Silberrad and R. Farmer, J. S. C. I. 1906, **25**, 961; 1907, **26**, 35; Zts. Schiess. Spreng. 1906, **1**, 405; 1907, **2**, 61, 84; abst. C. A. 1907, **1**, 358; J. C. S. 1906, **89**, 1182, 1759; Mon. Sci. 1908, **68**, 36; Chem. Centr. 1906, **77**, II, 1046, 1723; 1907, **78**, I, 538; Meyer Jahr. Chem. 1906, **16**, 325; 1907, **17**, 313.

likely to occur at low temperature, and a truer estimation of stability is recorded.

Other Stability Tests. Whereas most stability tests depend on the behavior of the powder when subjected to heat, a test by A. Weirman[1] is based on the observation that nitrocellulose colloids in an unstable condition absorb moisture from the air more readily than do stable colloids. The test, however, is very limited in its application, and at most only gives a record of the substance at the time of the test. Freshly made smokeless powder contains very little moisture, but the gradual loss of the residual solvent during storage renders the colloids more hygroscopic; the absorbed moisture in a powder may serve as an index of its stability. About ten grams of the powder (whole grains) are weighed, dried 7 days in a desiccator over sulfuric acid and loss noted. The dried sample is then exposed for about two days to an atmosphere saturated with water until its weight becomes constant, the temperature of each test being preferably the same. This increase in weight plus the above loss in weight equals the moisture range, which, corrected for surface moisture, gives comparable results for all sizes of grains. Since nitrocelluloses of varying nitrogen content have varying affinities for moisture,[2,3] the above test will only be applicable in the restricted examination of special samples of nitrocellulose of similar nitrogen content.

A. Angeli assumes that the stability of an explosive is related to the amount of acid present in the explosive.[4] He measures the acidity by the aid of the indicator dimethylaminoazobenzene,[5] which becomes red in presence of acid. In 1864 C. De Luca[1] showed that the nitrocellulose produced in that period decomposed more rapidly when exposed to sunlight than in diffused light, while in darkness he claimed that the decomposition was very slow. The observations of De Luca were made at a comparatively low temperature (50°). The decomposition in the sample exposed (at 50°) to sunlight was complete and took place in several stages. In 1867 F. Abel[2] also investigated the action of sunlight on nitrocellulose. With a stable dry guncotton he found that the action of light was very small. Guncotton containing some moisture when exposed to light decomposes very slowly with the formation of nitrates, nitrites and other compounds. The action, however, is very slow and is not suitable as the basis of a quantitative stability test.

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[1] Eighth Inter. Cong. Appl. Chem. 1912, **4**, 157; abst C. A. 1912, **6**, 3520; J. S. C. I. 1912, **31**, 905.

[2] C. Beadle, Chem. News, 1894, **70**, 247; abst. Chem. Centr. 1895, **66**, I, 1[illegible]8; Jahr. Chem. 1894, **[illegible]7**, 2230; Bull. Soc. Chim. 1895, **14**, 143.

[3] Haller, Les Ind. Chim. **2**, 420.

[4] Atti. accad. Lincei, 1918, **27**, I, 164; abst. C A. 1919, **13**, 262; J. S. C. I 1918, **37**, 608-A.

[5] This forms red salts, which become fixed to the surface of the explosive as a dyestuff does to a fiber A few cc. of distilled water containing 3 or 4 drops of a 0.2% alcoholic solution of the indicator are poured on to about 0.5 gm. of the powder, the whole being well stirred. Powder of good quality turns lemon-yellow, whereas, if more or less acidity is present, it becomes more or less intensely red, in either case, the supernatant liquid remains completely colorless. Not all explosives which are acid show low stability when subjected to the heat test, but experiment demonstrates that they inflame far more readily than normal explosives when kept in large amounts at a relatively high temperature, and they also burn irregularly and incompletely, and in the firing test exhibit abnormalities in the pressure and range. A dilute solution of the above indicator may be used for reveal-

D. Berthelot and H. Gaudechon[3] have shown that the action of the ultra-violet rays on various explosives is to accelerate those changes in composition which tend to occur spontaneously in the lapse of time, hence those alterations which are produced in the course of years by the natural agent of heat, humidity and contact of air may be made to occur within a few hours. Obviously, therefore, an examination by the ultra-violet rays offers a means of testing the stability of various explosives, their condition at any given time and their rate of deterioration. "Ultra-violet-rays" test, however, has not been completely worked out. It can at most only be used as a confirmatory test to the usual tests. Against the test is the point that the treatment in this stability test differs entirely from the treatment that the explosive will receive in actual storage. They exposed the explosive in thin quartz tubes containing mercury and an atmosphere of nitrogen to rays from a mercury vapor lamp.[4] Nitroglycerol was found to evolve carbon dioxide, carbon monoxide, nitrogen, nitrous ox-

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ing the effect of light on smokeless powder; the parts of the latter which have been exposed are turned red by the solution, whereas the other parts become yellow.

[1] Compt. rend. 1864, **59**, 487; abst. Dingl. Poly. 1864, **174**, 388; Wag. Jahr. 1864, **10**, 243; Mon. Sci. 1864, **12**, 951; Poly. Centr. 1865, **31**, 197; Jahr. Chem. 1864, **17**, 570.

[2] Phil. Trans. Roy. Soc. 1867, 181. Second memoir on nitrocellulose, which see.

[3] Compt. rend. 1911, **153**, 1220; C. A. 1912, **6**, 804, 1225, 2530; J. S. C. I. 1912, **31**, 47; Chem. Zentr. 1912, **83**, I, 534.

[4] Compt. rend. 1912, **154**, 201; C. A. 1912, **6**, 1225, 2530; Zts. Schiess. Spreng. 1912, **7**, 52.

ide and nitric oxide. The mixed gases contained as much as 40% nitric oxide. Collodion nitrocotton gave a similar mixture with much less nitric oxide but showed less stability than French service powders, which yielded no oxides of nitrogen in former tests by D. Berthelot. In tests of two service powders (6 years old), one stabilized with diphenylamine, the other with amyl alcohol, the former yielded gas containing 14% nitric oxide, the other 1.7% nitric oxide at 75° and 20 mm. from source of light, while both gave no nitric oxide at a greater distance and lower temperature. In the first instance, decomposition was too rapid to be prevented by the stabilizers. The high amount of nitric oxide probably resulted from the decomposition of the nitrosodiphenylamine formed during the six years of life of the powder. Other stabilized service powders gave no nitrous gases. Experiments were also conducted to determine the stability of powder by means of the relative action of $N/10$ potassium hydroxide solution on the powder for a period of 30 minutes at various temperatures, the excess of alkali remaining being titrated with acid.

A special apparatus suitable for the test of exposing explosives to ultra-violet light has been devized by M. Guilbaud.[1] It consists essentially of a transparent quartz tube, 100 mm. long and 15 mm. diam., in which the material to be decomposed is placed. The decomposition tube is closed by a ground glass cap, from which a short, narrow tube, fitted with a three-way stopcock leads to a measuring burette. About 2 to 2.5 grams of the nitrocellulose or powder to be tested is placed in the decomposition tube and the tube evacuated (20 mm.). The tube is then exposed to the rays of a mercury vapor lamp and the quantities of gas evolved during definite periods are noted for construction of the velocity curve of decomposition. The gas collected is then analyzed. The decomposition of nitrocellulose and smokeless powders produces five gases, i. e., CO_2, CO, N_2, N_2O and NO, in varying proportions.

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[1] Compt. rend. 1915, **161**, 212; abst. J. S. C. I. 1915, **34**, 984; C. A. 1915, **9**, 2982; J. C. S. 1915, **108**, ii, 706; Bull. Soc. Chim. 1916, **19**, 93. In the determination of mineral residue in smokeless powders according to C. Lutri (Giorn. chim. ind. applicata, 1920, **2**, 244; abst. C. A. 1920, **14**, 2711), the powder is cut or rasped to a coarse powder, and 0.5 gm. treated with 1 gm. pyridine in a porcelain crucible for one half hour, followed by heating on a water bath, evaporated and treated with three successive portions of 10 drops of pyridine, evaporating before each addition. The residue is then dark brown, of syrupy consistency and suffused with bubbles. This is treated several times with five drops of water, evaporating each time as before, until the residue is carbonaceous. The material is then heated first in an air bath, then more strongly until bubbles cease to develop and finally to incandescence over a free flame. The method is claimed to have given good results with ash up to 8%. Graphite can be determined in a somewhat similar manner, taking 5 gm. of the powder.

United States Ordnance Methods for Testing Nitrocellulose. The most recent official methods of conducting these determinations are as follows:

65.5° C. Heat Test with Potassium Iodide Starch Paper. The sample shall be pressed in a clean cloth or wrung in a wringer if it contains a large excess of water. The cake shall be rubbed up in the cloth until fine, taking care that it does not come in contact with the hands, spread out on clean paper trays, and dried in an air bath at 35° to 43° C. just a sufficient length of time to reduce the moisture to that amount which will give a minimum heat test, this amount being from 1.5% to 2%. If, as sometimes happens in dry weather, the moisture has been reduced to less than 1.5%, the sample shall be placed in a moist atmosphere for a time not exceeding 2 hours, until the required moisture percentage is obtained. The whole time of drying and making the test shall not exceed 8 hours.

The dried sample for the heat test shall be weighed out in five test tubes, 1.3 grams (20 grains) to each tube, so that a series is obtained covering the widest variation allowed for moisture. These tubes are standard, $5^1/_2$ inches long, $^1/_2$ inch internal diameter, and $^5/_8$ inch external diameter, closed by a clean cork stopper, fitting tightly, through which passes a tight glass rod with platinum holder for the paper. Corks are discarded after one test. The nitrocellulose is pressed or shaken down in the tube until it occupies a space in the tube of $1^6/_8$ inches. The test paper, about 1 inch in length and $^3/_8$ inch wide, is hung on the platinum holder, and moistened on its upper half with a 50% solution of pure glycerol in water. The heating bath, carefully regulated at 65.5° C. ± 1° C., is placed so that a bright reflected light is obtained and tube placed in the bath. Time is marked when tubes enter bath. As test continues a slight film of moisture condenses on inside of tubes, and the line of demarcation between wet and dry test paper is kept abreast the lower edge of the moisture film. The first appearance of discoloration of the damp portion of the test paper marks the end of the test for each separate tube, the minimum test of any one of the five tubes being the heat test of the nitrocellulose. This discoloration is to be greater than that obtained at the same time by a blank test.

Standard test papers will be used and will be furnished by the department to manufacturers.

The standard water bath holds 10 tubes and is made long and narrow to reduce to a minimum the heating of the upper portions of the tubes. These tubes are immersed in the bath to a standard depth of 2.25 inches.

135° C. Test. A sample of nitrocellulose is laid out in paper trays and dried for 4 to 5 hours at 42° C., or is dried over night at room temperature and then further dried one-half hour at 42° C., after which 2.5 grams are pressed into the lower 2 inches in each of two tubes, of heavy glass, about 290 mm. long, 18 mm. outside diameter, and 15 mm. inside diameter, closed with a cork stopper through which a hole 4 mm. in diameter has been bored. A piece of standard normal methyl violet paper, 70 mm. long and 20 mm. wide, is placed in each tube, its lower edge 25 mm. above the cotton. When the constant temperature bath has been carefully regulated at 134.5° C. ± 0.5° C., these tubes are placed in the bath so that no more than 6 or 7 mm. of length projects from bath. Examination of the tube is made by withdrawing about one-half its length and replacing quickly each 5 minutes after 20 minutes have elapsed. The methyl violet test paper in either tube shall not be completely turned to standard salmon-pink in less than 30 minutes.

Standards for salmon-pink to be furnished by the Government.

The bath must be placed in a good light, with a suitable background.

There shall be no failure of either of the tubes.

The standard normal methyl violet papers will be furnished by the department.

Nitrogen Content. Nitrogen content is determined on a 1-gram sample of nitrocellulose dried to constant weight at a temperature between 98° and 102° C., or in a vacuum drier after a thorough air drying.

The nitrocellulose is washed into a DuPont nitrometer by

20 cc. of H_2SO_4. The per cent. of nitrogen is read by comparison of gas given off with a standard volume.

The nitrometer is standardized by preparation of a standard volume of dry air calculated to a temperature of 200° C. and 760 mm. pressure in the comparison tube.

When pure potassium nitrate is tested with the standard sulfuric acid against such comparison tube the nitrogen figure should invariably be 13.85%.

The acid used shall be chemically pure sulfuric acid containing 95% ±0.3% H_2SO_4.

Ash. This is determined by decomposition with nitric acid, ignition, and weighing the residue.

Ether-Alcohol-Insoluble Material. The percentage of ether-alcohol-insoluble material in the nitrocellulose as used in these specifications shall be determined as follows: Soak 1 gram of the dry sample for two hours in 50 cc. of 95% alcohol in an Erlenmeyer flask. Then add 100 cc. of ethyl ether, shake and allow to stand over night. On the following morning the mixture is shaken thoroughly and transferred to a specially constructed solubility tube of the following dimensions: Total length, 21 inches; inside diameter, 1.35 inches; the lower end constricted for a distance of 2 inches to an inside diameter of 0.3 inch and graduated in one-tenth cc. to 10 cc. The constricted portion should be tapered gradually from the large part of the tube and the graduations should extend to the top of the shoulder thus formed. After standing for seven hours in the solubility tube, the volume occupied by the insoluble and semisoluble matter is read in cubic centimeters from the scale on the tube. This number (of cubic centimeters) multiplied by 0.5 is the percentage of ether-alcohol-insoluble matter as used in these specifications.

The official temperature for this determination shall be 15.5° C., and in case of doubt or for greater accuracy the complete determination shall be made at this temperature, the solvents being brought to this temperature before their addition to the sample.

Factor of Solubility. The solubility of nitrocellulose being very difficult of determination, an arbitrary "factor of solubility" is used to define acceptability of nitrocellulose in this respect. This factor of solubility for nitrocellulose is obtained by subtracting from 100% the sum of the percentages of ash and ether-alcohol-insoluble material, determined as prescribed in the determination of ash and ether-alcohol-insoluble material.

Guncotton Specifications in Great Britain. The following, it is understood, are substantially the specifications under which nitrocellulose especially suitable for the manufacture of cordite, is produced in Great Britain.

1. The nitrocellulose should be equal to that manufactured at the Royal gunpowder factory at Waltham Abbey.

2. If the nitrocellulose is made by the displacement process, the period of nitration should not be less than $2^1/_2$ hours. It should be subjected to two boilings of 12 hours each, directly as it comes from the cold water washing after nitration, the first boiling being in an acid solution approximating 1% of acid on the weight of the guncotton; this amount of acid being normally disengaged from the nitrocellulose. The second 12-hour boiling should be in slightly acid solution. This should be followed by 4 boilings of 4 hours each, and one of 2 hours, in water with an alkalinity equivalent to about 270 parts of calcium carbonate per million, any deficiency in alkalinity of the natural water being made up by the addition of sodium carbonate. If a hard water is used, it may be found that the required residual calcium carbonate has been deposited in the fiber; if not, the deficiency is corrected by the addition of precipitated calcium carbonate during the poaching, or by precipitating the $CaCO_3$ in the fiber by the use of calcium hydroxide, followed by sodium carbonate, any soluble alkali being washed out by means of water.

The removal of iron and grit should, in the main essentials follow the methods as used at Waltham Abbey.

3. The nitrocellulose must be free from un-nitrated cotton, and from all extraneous matter not permitted by the specifications.

4. The guncotton must be free from grit and from any other mineral matter other than that unavoidably taken up by the nitrocellulose from the wash water and machinery used in manufacture, or naturally present in the cotton; the total quantity of mineral matter, as determined by ashing a suitable quantity of the material with due precautions and sulfating the ash, not to be in excess of 1%.

5. The nitrocellulose must contain from 0.2% to 0.4% of

calcium carbonate, calculated to the dry basis, the estimation of this ingredient being carried out along the following lines:

Ten grams of guncotton are shaken in a tall glass cylinder with 100 cc. of $N/10$ HCl diluted with an equal amount of distilled water, for one hour, and allowed to settle for the same period; after which 100 cc. of the clear supernatant liquid are removed by a pipette and titrated with $N/10$ sodium carbonate, with methyl orange as an indicator, the alkalinity of the sample being calculated in terms of $CaCO_3$ on the dry guncotton.

6. The percentage of nitrogen, as calculated on guncotton free from mineral matter, should be not less than 12.9% nor more than 13[illegible]%, the estimation being carried out as follows:

From 0.5 to 0.52 gm. of perfectly dry guncotton (obtained from the poachers before alkaline matter is added, and dried) is weighed in a stoppered weighing bottle; 5 cc. of pure 96% sulfuric acid are added and stirred until complete disintegration has taken place and the mixture can be readily poured into a 150 cc. nitrometer. The weighing bottle and cup are washed out with 9.5 cc. of sulfuric acid, divided into several portions, 0.5 cc. distilled water being added to the last portion. The nitrometer is then shaken to effect the reaction, and when the same is completed and the temperature of the apparatus has become stable, the volume of NO disengaged is read off, reduced to standard conditions of 0° and 760 mm. pressure and the percentage of nitrogen in the sample calculated.

7. The percentage of nitrocellulose soluble in ether-alcohol, should not be in excess of 12% as calculated on the dry nitrocotton. To determine this, 4 gm. of dry guncotton are shaken with 200 cc. of a mixture of 2 parts (by volume) of pure ethyl ether and 1 part of alcohol (sp. gr. 0.830) for six hours, at intervals of about 15 minutes, the insoluble matter being then allowed to subside. When clear, 75 cc. of the supernatant solution are transferred to a weighed flask, the solvent is evaporated, and the residue dried to constant weight at a temperature not in excess of 65°. The solution should be made at a constant temperature of 15.5°.

$$\frac{\text{Wt. of residue} \times 100}{1.5} = \%\ \text{of soluble nitrocellulose in sample.}$$

8. The percentage of organic matter insoluble in acetone is

not to be in excess of 1% on the dry guncotton. The total amount insoluble in acetone is determined, and the loss on ignition after conversion of the ash to carbonates, is calculated as the "organic matter insoluble in acetone."

9. The total amount of sulfate as calculated to H_2SO_4 on the dry nitrocellulose must not exceed 0.1%, the determination being carried out as follows:

Five gm. guncotton are dissolved in 50 cc. of nitric acid (sp. gr. 1.5), a few crystals of potassium chlorate being added when solution is complete, and the solution evaporated almost to dryness over a small flame. The concentrated solution is then treated with 5 cc. HCl and 0.5 gm. potassium chlorate in successive small portions and again evaporated almost to dryness, this treatment being once repeated, the residue dissolved in water, filtered, and the sulfuric acid estimated as $BaSO_4$, precipitated from about 150 cc. of liquid. A blank determination on the reagents is also made, and any $BaSO_4$ thus found subtracted from the result.

10. The heat test follows the usual lines, as previously described.

11. The nitrocellulose, when subjected to the Will test,[1] should give off not more than 6.5 mgm. of nitrogen in four hours from 2.5 gm. of material.

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[1] R. Robertson. J. S. C. I. 1902, **21**, 81[illegible]; abst. Mon. Sci. 1903, [illegible], 658; Chem. Centr. 1902, **73**, II, 940; Jahr. Chem. 1902, **55**, 1055.